

Wisconsin Urban Air Toxics Monitoring

**A Summary Report for the Period
July 1997 - June 1998**

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EXECUTIVE SUMMARY	1
RESULTS OVERVIEW	2
SAMPLING AND ANALYTICAL PROCEDURES.....	4
SEMI-VOLATILE ORGANIC COMPOUNDS: POLYCHLORINATED BIPHENYLS AND PESTICIDES.....	4
POLAR ORGANIC COMPOUNDS: CARBONYLS	4
VOLATILE ORGANIC COMPOUNDS	5
TOTAL SUSPENDED PARTICULATE AND METALS	5
TOTAL SULFUR AND SULFUR DIOXIDE	5
QUALITY ASSURANCE OBJECTIVES.....	5
SEMI-VOLATILE ORGANIC COMPOUND PARAMETERS	7
OVERVIEW	7
PARAMETER SOURCES AND USES.....	7
DATA COMPLETENESS	9
ANALYTICAL RESULTS	10
QUALITY ASSURANCE PARAMETERS.....	12
INTER SITE COMPARISON.....	12
GREEN BAY PCB AND PESTICIDE TREND ANALYSIS.....	14
PCB AND PESTICIDE PARAMETER CONCLUSIONS	18
NON-VOLATILE METAL PARAMETERS.....	19
OVERVIEW	19
PARAMETER USES AND ATMOSPHERIC SOURCES	19
REPORTED EMISSIONS	21
CURRENT TSP AND METALS.....	24
<i>Data Completeness.....</i>	24
<i>Analytical Results.....</i>	24
<i>Additional Metal Samples.....</i>	26
<i>Site Intercomparison</i>	27
QUALITY ASSURANCE PARAMETERS.....	29
<i>Data Representativeness</i>	30
INORGANIC PARAMETER CONCLUSIONS.....	32
CARBONYL PARAMETERS.....	33
OVERVIEW	33
PARAMETER USES AND ATMOSPHERIC SOURCES	33
REPORTED EMISSIONS	35
CURRENT WUATM FORMALDEHYDE	37
<i>Data Completeness.....</i>	37
<i>Analytical Results.....</i>	38
QUALITY ASSURANCE PARAMETERS.....	40
CARBONYL COMPOUND CONCLUSIONS.....	42
VOLATILE ORGANIC COMPOUNDS.....	43
OVERVIEW	43
VOLATILE ORGANIC COMPOUNDS, DATA COMPLETENESS.....	43
VOLATILE ORGANIC COMPOUNDS, TOXICS ANALYTICAL RESULTS	43
VOLATILE ORGANIC COMPOUNDS, QUALITY ASSURANCE PARAMETERS	45
VOC DATA COMPARISONS	47
PARAMETER.....	48
VOLATILE ORGANIC COMPOUND CONCLUSIONS	48

SULFUR GASES.....	49
OVERVIEW	49
PARAMETER SOURCES	49
REPORTED EMISSIONS	50
SULFUR GAS RESULTS SUMMARY	53
SULFUR GAS CONCLUSIONS	58
RECOMMENDATIONS	59
SEMI-VOLATILE ORGANIC COMPOUNDS	59
STATEWIDE METALS	59
REFERENCES.....	60

Executive Summary

The Clean Air Act Amendments of 1990 define an approach to Hazardous Air Pollutants (HAPS) which includes seeking a substantial reduction in emissions and public health risks associated with exposures. As a part of this, a research program is outlined which includes ambient monitoring for a broad range of HAPs in a representative number of urban locations.

The Wisconsin Urban Air Toxics Monitoring Network (WUATM) was conceived in response to these directives. The WUATM is intended to provide information for the following uses:

- ▶ Determine concentrations of HAPs in Wisconsin's Urban Atmospheres
- ▶ Assess Potential Air Toxics Problems
- ▶ Background Data and Trend Analysis
- ▶ Fate of Air Toxics
- ▶ Evaluation of Sampling and Analytical Methods

The full network was originally planned to consist of 4 or 5 monitoring stations located throughout the state. A single prototype site was established in Green Bay during 1991. This site was moved to a second location within Green Bay during 1993 in response to concerns that the original site did not adequately represent local air quality.

The WUATM was expanded in July 1996, with the addition of 4 other sites for the non-volatile metal parameters. Sampling frequency for these elements was reduced from once every six days to once per month, as the available funding for this purpose did not increase. Additional funding from the EPA was received in January 1997 to allow for toxic VOC analysis at an existing Milwaukee site.

Most sampling in Green Bay (with the exception of PCBs and pesticides) was discontinued in June, 1997, and the site moved to Wisconsin Rapids. The site was established with the cooperation of the City Parks Commission at Witter Field, located near the geographic center of town. This report contains the first year's data from the Wisconsin Rapids site, along with July 1997 through June 1998 data from the statewide metals, Green Bay PCB and Milwaukee VOC programs. Formaldehyde results obtained from the Photochemical Assessment Monitoring (PAMS) effort in Milwaukee have been incorporated to provide additional comparison data.

This monitoring is designed to be a screening program to determine concentrations of organic and inorganic compounds present in Wisconsin's urban air. The program is considered to be a screening program because only a limited number of compounds have been collected and quantified. Most of these compounds are listed in Table 1 below. In general, the compounds can be grouped as semi-volatile organic compounds (including PCBs and pesticides), polar organic compounds (formaldehyde), volatile organic compounds and non-volatile metals.

Site specific concerns in the Wisconsin Rapids area include sulfur gases and methanol produced by the paper mills in the area. Two continuous monitoring parameters, sulfur dioxide (SO₂) and total sulfur, were added in response to these concerns. Data has been collected on a minute average basis since December 1997 to maximize the information available about transient pollution events. Attempts to develop a method for methanol have been unsuccessful to date.

Table 1: Parameter List for Wisconsin Urban Air Toxics Monitoring Program, 1996 - 97		
SEMI-VOLATILE ORGANIC COMPOUNDS		TOTAL PCBS (Aroclor)
ATRAZINE	HEPTACHLOR EPOXIDE	cis-NONACHLOR
DDE	LINDANE	trans-CHLORDANE
DIELDRIN	cis-CHLORDANE	trans-NONACHLOR
NON-VOLATILE METALS		SELENIUM
ARSENIC	CHROMIUM	VANADIUM
CADMIUM	LEAD	TSP (µg/M3)
CARBONYL COMPOUNDS		
ACETALDEHYDE	ACETONE	FORMALDEHYDE
VOLATILE ORGANIC COMPOUNDS		METHYLCHLORIDE
1,1,1-TRICHLOROETHANE	BROMODICHLOROMETHANE	METHYLENE CHLORIDE
1,1,2,2-TETRACHLOROETHANE	BROMOFORM	n-OCTANE
1,1,2-TRICHLOROETHANE	BROMOMETHANE	o-XYLENE
1,1-DICHLOROETHANE	c-1,3-DICHLOROPROPENE	PROPENE
1,2-DICHLOROBENZENE	CARBON TETRACHLORIDE	STYRENE
1,2-DICHLOROETHANE	CHLOROBENZENE	t-1,2-DICHLOROETHENE
1,2-DICHLOROPROPANE	CHLOROETHANE	t-1,3-DICHLOROPROPENE
1,3-DICHLOROBENZENE	CHLOROFORM	TETRACHLOROETHENE
1,3 BUTADIENE	CHLOROPRENE	TOLUENE
1,4-DICHLOROBENZENE	CUMENE (i-PROPYLBENZENE)	TRICHLOROETHENE
ACETYLENE	DIBROMOCHLOROMETHANE	VINYLCHLORIDE
BENZENE	ETHYLBENZENE	XYLENES (m & p)
SULFUR GASES	SULFUR DIOXIDE	TOTAL SULFUR

Results Overview

Polychlorinated biphenyl (PCB) and pesticide samples were collected in both Wisconsin Rapids and Green Bay. PCB values average 0.25 ng/m³ in Green Bay, and 0.15 ng/m³ in Wisconsin Rapids. These values are somewhat lower than observed at the former Fox River HAP station in Green Bay. A distinct seasonal trend is apparent in both sites, with summer values significantly greater than all other seasons. Atrazine and lindane are also detected periodically.

Formaldehyde values in Wisconsin Rapids range from 0.35 ug/m³ to 1.78 ug/m³, with an average of 0.77 ug/m³. Formaldehyde is monitored elsewhere in the state as part of the

Photochemical Assessment Monitoring (PAMS) program. Values from Milwaukee range from $0.03 \mu\text{g}/\text{m}^3$ to $8.22 \mu\text{g}/\text{m}^3$, with an average of $3.07 \mu\text{g}/\text{m}^3$.

A variety of volatile organic compounds considered Toxics have been detected in the atmosphere of Wisconsin Rapids. Detected values have ranged from 0.05 ppbv to 3.3 ppbv (maximum value for acetylene). The average values for all parameters other than acetylene are less than 1 ppbv (average acetylene value is 1.03 ppbv). Samples in Milwaukee have been collected since January 1997. Detected values have ranged from 0.05 to 7.90 ppbv (maximum value for acetylene). The average values for all parameters other than acetylene are less than 1 ppbv (average acetylene value is 1.89 ppbv).

A suite of 6 metals, (arsenic, cadmium, chromium, lead, selenium and vanadium), have been sampled at 5 locations statewide. Values tend to increase in larger urban areas. Results obtained from Wisconsin Rapids show that average concentrations are similar to the background site at Trout Lake, with the exception of lead, which is slightly elevated above the background levels.

Recommendations regarding continued operations and expansion of the toxics monitoring network fall into two basic categories: further refinements of methods, and expanding the network to different localities. Suggestions for the continued expansion and refinement of the Urban Air Toxics Monitoring Program are included at the end of this report.

Sampling and Analytical Procedures

Sampling and analytical procedures for all parameters are specified in the Hazardous Air Contaminants Fixed Urban Site Monitoring Program Quality Assurance Project Plan (QA 8.0) prepared by DNR personnel in 1991. Specific methods are documented in the DNR Air Monitoring Handbook.

Semi-Volatile Organic Compounds: Polychlorinated Biphenyls and Pesticides

PCB and pesticide samples are collected using a General Metal Works PS-1 sampler loaded with a combination quartz filter and polyurethane foam (PUF) plug, following EPA TO-4 protocols as outlined in DNR OP 8.5, Sampling Semivolatile Organic Compounds Using a PS-1 Sampler. Air is drawn through the sampler at the maximum possible rate. This rate varies from slightly over 8 CFM to as much as 9.5 CFM, depending upon the condition of the sampler motor and the density of the PUF plug.

The initial sampling protocol called for a 72 hour sampling period. This was changed for winter months in November 1995 to a 144 hour period because of a lack of results under the shorter sampling time. The 144 hour sampling period was achieved through 2 separate 3 day sampling periods following the every 12 day sampling schedule. The samples were stored at about 4°C inside their original sampling heads with the ends sealed using Parafilm between the sampling periods. Summer and fall protocol remained with the 72 hour sampling period.

Following collection of the sample, the filter and PUF plug are packed in hexane rinsed aluminum foil and shipped to the laboratory for analysis. Analysis for these parameters is performed at the State Lab of Hygiene (SLOH). PUF plugs and filters are extracted with 5% ethyl ether/hexane and brought to a final volume of 1 ml. The extracts are analyzed by gas chromatography with an electron capture detector to determine the presence of selected chlorinated compounds. Confirmation of compounds is through the routine use of dual column analysis, with occasional mass spectroscopy.

Polar Organic Compounds: Carbonyls

Carbonyl samples are collected by drawing a known volume of ambient air through commercially prepared cartridges containing 2,4-dinitro phenylhydrazine (DNPH) coated silica gel, following EPA TO-11 as outlined in DNR OP 8.4, Aldehyde Sampling with 2,4-Dinitro phenylhydrazine impregnated sampling cartridges. Aldehydes react with the DNPH to form stable derivatives which can then be analyzed. Samples are collected over a 24 hour period at a rate of approximately 700 cc/min. Following collection, samples are refrigerated until shipment to the laboratory.

Aldehyde samples are analyzed at WOHL. The exposed cartridges are washed with acetonitrile to remove the aldehyde-DNPH derivatives. The eluant is brought to a known volume and then analyzed at the Wisconsin Occupational Health Laboratory (WOHL)

using reversed phase HPLC coupled with UV absorption detection.

Volatile Organic Compounds

Sampling and analysis of VOCs follows the protocols of EPA TO-14 employing passivated stainless steel canisters. A low flow 24 hour sample is collected in an evacuated canister, which is then sent to the laboratory for cryogenic concentration followed by high resolution gas chromatography with mass spectroscopic detection. The analysis was performed at Biospheric Research Corporation in Hillsboro, Oregon through December 1996, at which point the SLOH Environmental Studies Unit took over this task.

Total Suspended Particulate and Metals

Standard high volume methods as documented in DNR OP.1.2, High Volume Sampler, are employed at the Green Bay Toxic monitoring sites for the collection of TSP samples. A 24 hour sample is collected on a pre-weighed glass fiber filter at an average flow rate of 1.42 m³ per minute. Filters are sent to the SLOH for determination of total mass of particulate collected. The same sample is used for determination of ambient concentrations of non-volatile metals. The metals are determined by digesting a portion of the filter in acid and analyzing the resulting solution using atomic absorption spectroscopy.

Total Sulfur and Sulfur Dioxide

Sulfur parameters are continuously monitored using Monitor Labs (ML) 8850 sulfur dioxide analyzers. The method of detection for these instruments is UV fluorescence, wherein the sampled gas stream is passed through a chamber bathed with UV light, which excites the SO₂ molecules and causes them to emit energy in a characteristic wave band. As this method of detection is specific to SO₂, the total sulfur analyzer employs an oxidation catalyst in line prior to the ML 8850 to convert all reduced sulfur compounds to SO₂. Operations and method details are located in DNR OP.2.6, Sulfur Dioxide - Monitor Labs 8850 Analyzer.

Data is collected on a minute average basis using a computer based DNR logger. Comparison of the two values, (SO₂ and total sulfur), are made to discern periods with potentially distinguishable reduced sulfur compounds. Extra effort goes into maintaining the instruments far within method specified quality control limits, to allow this type of comparison validity.

Quality Assurance Objectives

Several aspects of quality control and assurance protocols have been incorporated into the WUATM. The quality assurance objectives are precision, accuracy, completeness, representativeness and comparability.

Precision for discrete samples is determined by means of quarterly duplicate samples. The

goal is for the duplicates to be within $\pm 15\%$ for each individual parameter. Precision of continuous parameters is determined through a bi-weekly check in which the analyzers are challenged with known concentrations of SO_2 and H_2S . Although the formal QC limit set forth in OP 2.6 is $\pm 10\%$, considerable effort has gone into maintaining the instruments well within the $\pm 5\%$ range.

Accuracy is intended to be determined on two levels, that of sampling using air flow audits, and also analytical accuracy through submission of spiked samples. Sampler audits are performed yearly by personnel other than the regular site operator, with the goal being to have the actual flow rate within $\pm 10\%$ of the expected sampling air flow rate. Yearly audits of continuous monitors are conducted by personnel not associated with regular toxic site operations.

Analytical relative accuracy determinations are made by submitting samples spiked with representative compounds. These samples are occasionally available from EPA and other sources. Several of these samples were submitted. In addition, spiked media recovery determinations are a typical part of the analytical in-house quality control mechanism. The goal for accuracy determinations are for the results to be within $\pm 25\%$ of the actual amount introduced to the media.

The completeness parameter involves trying to obtain valid samples for all scheduled sampling days. Monitoring plans call for sampling metals every 6 days. All other parameters were sampled on an off-set every 12 days schedule. Continuous parameters are evaluated on a minutes per month basis for completeness.

Representativeness is accomplished through meeting the criteria for sampling locations set forth by USEPA in the Compendium of Methods for the Determination of Toxic Organic Compounds and 40 CFR Part 58, Appendix E. Comparability involves reporting data in units consistent with other organizations reporting similar data. In general, volatile compounds are reported in part per billion volume (ppbv), while semi-volatile and non-volatile compounds are reported in micrograms or nanograms per cubic meter (ug/m^3 or ng/m^3).

Semi-Volatile Organic Compound Parameters

Overview

The primary semi-volatile organic compound parameters incorporated into the WUATM study at the current time are PCBs, some chlorinated pesticides and atrazine. Samples are collected from the Prange Way site in Green Bay (55-009-0009) and Witter Field in Wisconsin Rapids (55-141-0016).

All data collected between July 1997 and June 1998 is included in this report. Statistical analysis of PCB data collected to date is presented for determination of between site differences, and yearly and seasonal trends. Background information on parameter uses and atmospheric sources is also included.

Parameter Sources and Uses

This broad designation includes a wide variety of chemicals, both natural and synthetic. The compounds are generally slightly volatile oils or solids with a low affinity for water, and are represented by a wide variety of individual parameter groups. This variety poses numerous difficulties for an air sampling program. Different collection and analytical methods are suited for different compound classes. Also, many chemicals of potential interest do not have proven methods for their determination in air.

Many of these compounds are persistent in the environment. This means that they are not readily degraded, and are available for continued cycling in the environment long after they are no longer in general use. Many different research groups are investigating the cycling of these pollutants through different environmental compartments (sediment, water, air and biota).

Atmospheric levels of all of these compounds tend to be very low, which makes them difficult to sample and analyze. The low levels present require large volumes of air to be sampled. The compounds may be either particle bound or exist as a vapor, which requires a combination of filtering and an adsorbent material to effectively capture the compounds. The variable volatility and adsorption characteristics may lead to sample loss. In addition, the quantity of other materials collected at the same time requires significant sample preparation and may interfere with analysis.

The approach adopted by WUATM has been to employ adsorbent sampling with polyurethane foam (PUF), coupled with a pair of analytical methods performed on the same sample. The first method uses a Nitrogen Phosphorus Detector (NPD) with Gas Chromatography (GC) to determine atrazine. The second method incorporates Electron Capture Detection and GC for the determination of PCBs and chlorinated pesticide parameters.

Polychlorinated biphenyls are a large group of closely related synthetic compounds generally associated with each other in complex mixtures. Individual components of these mixtures are known as “congeners”, of which there are about 200. Commercial mixtures were marketed under a variety of trade names, of which one of the more common were the various Arochlors. WUATM protocols quantify total PCBs by comparison with specific Arochlor mixtures. Profiles obtained in Green Bay and Wisconsin Rapids correspond to Arochlor 1242.

Prior to a ban in 1979, PCBs were used for a variety of purposes, from electrical transformer oil to carbonless copy paper and plastics. These uses led to wide dispersal throughout the environment, where they continue to persist. Old electrical equipment may still contain this pollutant.

The combination of chlorine, complex organic materials and heat may produce small quantities of PCBs and other complex chlorinated organic compounds. This phenomena has been shown for combustion of chlorine containing plastics in municipal incinerators, some paper bleaching processes, and automobile tailpipe emissions during winter in areas where salt is used to help clear roads. A few industrial sources report such emissions, generally in quantities of a few pounds per year or less.

Several areas in Wisconsin have been contaminated in the past, most notably the lower Fox River and Green Bay. These areas continue to provide sources of PCBs because of dispersal in sediment, water, air, flora and fauna. Current research indicates that environmental cycling is probably the largest source of this pollutant.

The various pesticide parameters come from a variety of both current and historical sources. These are primarily agricultural chemicals, although some have had widespread home use as well. Most of these parameters are chlorinated pesticides no longer in common use in the United States. Some of the parameters are degradation products of previously applied pesticides. Environmental cycling and global transport are the major atmospheric sources for most of these chemicals.

Atrazine is the most common agricultural pesticide in use today. The primary use is as a pre-emergent herbicide with corn and sorghum. It is a chlorinated nitrogen- containing synthetic organic compound of the triazine family. Other members of this family (simazine, and cyanazine) are also used extensively throughout the state. These chemicals are classed as probable human carcinogens. Cyanazine is being phased out by its primary manufacturer, with a total end to its production scheduled for 2002.

Atrazine is a “restricted use” pesticide. This designation means that application must be by, or under the supervision of, a licensed operator. This pollutant is mobile in the soil, and frequently found in groundwater, which can lead to the designation of local atrazine free zones. The 1996 Wisconsin Pesticide Use summary produced by the Wisconsin Agricultural Statistics Service reports that atrazine is used on about 50% of the total corn acreage in the state. Data from 1991 through 1996 is reported, showing a slight decline in the total amount applied, from over 2,000,000 pounds in 1991 and 1992 to 1,474,000

pounds in 1996.

DDE (dichloro-diphenyl-ethylene) is both a primary degradation product and synthetic contaminant of DDT (dichloro-diphenyl-trichloroethane). Both of these compounds continue to persist in the environment to some extent. Prior to domestic use being banned in 1979, DDT was widely used by cities for mosquito control. This use helped contribute to the deaths of many songbirds as documented in Rachel Carson's "Silent Spring". Studies have shown that general levels have decreased since that time, although these pesticides continue to be detected in the part per trillion range by some studies. Some global use of DDT continues today, including isolated spots in the US where there are small stockpiles.

Dieldrin is a chlorinated cyclodiene insecticide formerly used as for soil and seed treatment, and to control disease vectors such as mosquitoes and tsetse flies. Most uses were banned in 1975, and at present it is no longer produced in or imported into the United States. Another source of this chemical is environmental transformation of the closely related pesticide, aldrin, which was also banned in the mid-70's.

Lindane (γ -hexachlorocyclohexane) is still registered for a variety of uses both as the active ingredient in lice and scabies shampoos, and a variety of vegetable applications. This compound is not listed in the Wisconsin Pesticide Use summary cited above, which implies that there is negligible use in the state.

The remaining 5 parameters (heptachlor epoxide, cis - and trans - chlordane, and cis- and trans- nonachlor) are some of the primary components of technical chlordane, a complex mixture of chlorinated organic compounds widely used against ants and termites throughout the country. Use was severely restricted in 1983, and banned in 1988. Heptachlor epoxide is also a degradation product of a related pesticide, heptachlor, which was likewise banned in the early 1980's.

Data Completeness

PCB and pesticide samples were collected continuously throughout the testing period. Sampling frequency was dependent upon season, with 72 hour samples collected on a 1 in 12 day cycle between July and early November; 144 hour samples collected on a 1 in 24 day cycle between late November and early April; and 72 hour samples collected on a 1 in 12 day cycle for the remainder of the season.

Project completeness is documented in the following table. In this table, Completeness is the ratio of Ambient samples collected to total Sampling days. It should be noted that a single sampler is present at Prange Way, and no duplicate or spike attempts were made there.

Table 2: PCB and Pesticides Completeness

Site	Completeness	Samples	Voids	Ambient	Blanks	Duplicates	Spikes	Sample Days
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Prange Way	91.3%	27	5	21	1	0	0	23
Witter Field	91.3%	31	5	21	4	3	2	23

Analytical Results

Results of all samples were evaluated on the basis of maximum possible values in the case of non-detects, and actual values in the case of detected quantities. Only pesticide parameters which were detected are reported. Reporting limits of all chlorinated pesticides were raised during this sampling period because of difficulties associated with verifying low levels.

The tables below summarize results for all reported PCB and pesticide analytical parameters. Values are reported in ng/m³. PCB values are reported as Aroclor 1242. The number of pesticide samples differ from the PCB samples because analysis for these parameters is only performed between April and September.

Table 3: Green Bay PCB and Pesticide Results (ng/m³)

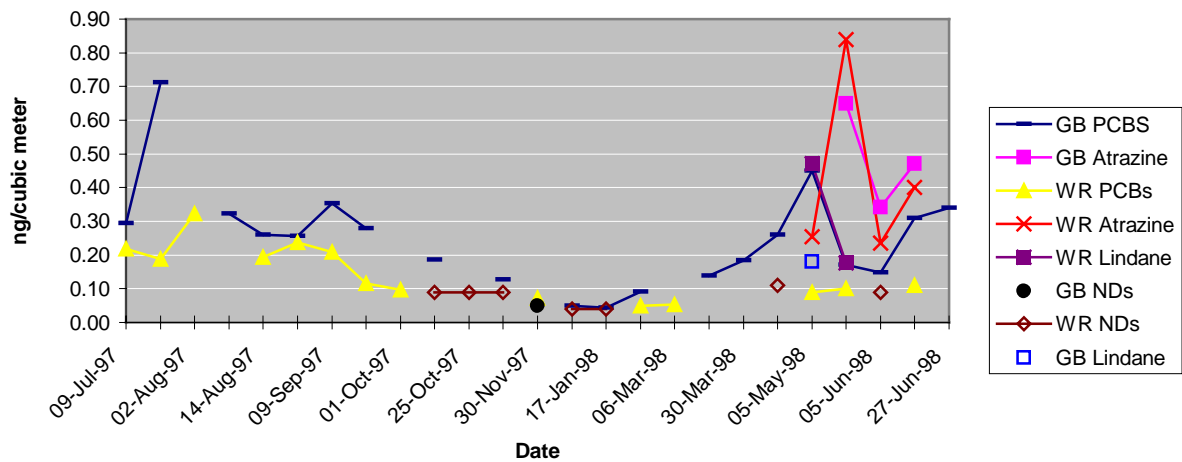
Parameter Name	Average	Maximum	Minimum	%RSD	Detects	Samples	Detection Rate
AROCLOR 1242	0.25	0.71	0.04	61.4%	20	21	95.2%
ATRAZINE	0.49	0.65	0.34	32.1%	3	13	23.1%
LINDANE		0.07			1	13	7.7%

Table 4: Wisconsin Rapids PCB and Pesticide Results (ng/m³)

Parameter Name	Average	Maximum	Minimum	%RSD	Detects	Samples	Detection Rate
AROCLOR 1242	0.15	0.32	0.05	53.3%	15	23	65.2%
ATRAZINE	0.39	0.84	0.20	66.5%	5	14	35.7%
LINDANE	0.12	0.18	0.07	64.9%	2	14	14.3%

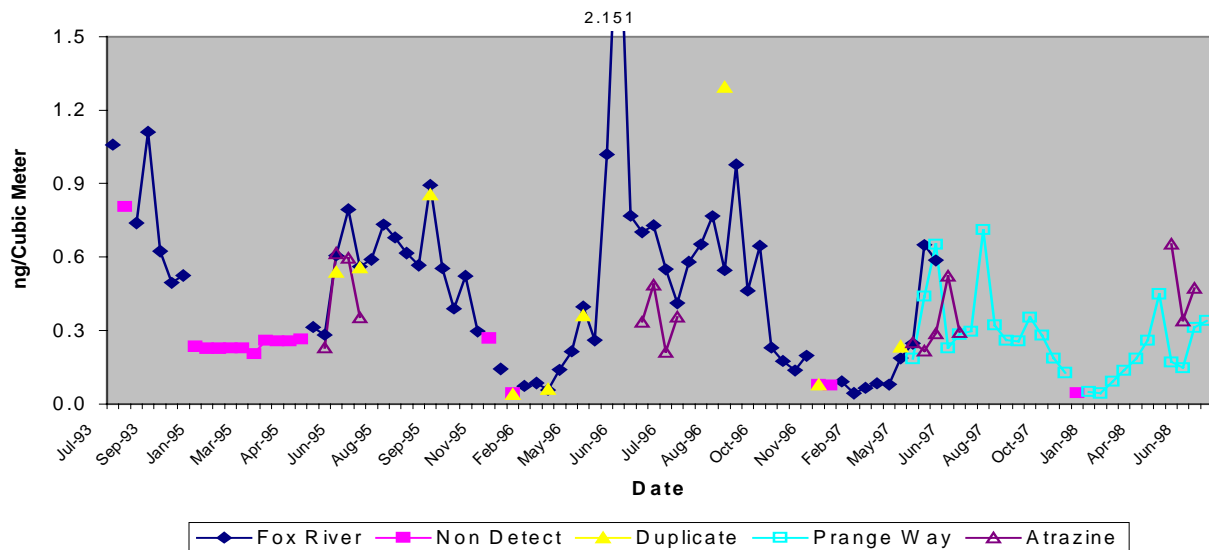
Results from the current sampling season are shown graphically below. “GB” refers to Green Bay, while “WR” refers to Wisconsin Rapids. The designation “ND” indicates samples which were non-detects. Pesticide non-detects are ignored in this graph. Note that not only are the Green Bay PCB values consistently higher than those in Wisconsin Rapids, but that considerably more non-detects were returned from the latter site.

Figure 1: PCB and Pesticide Results, 1997 - 1998



The following graph presents all Green Bay PCB data and pesticide detects from 1993 through the current season. The scale has been adjusted for the majority of the values, even though this places the highest value off-scale. Note the reduction in non-detects in 1995, and the consistent periodic detection of pesticides.

Figure 2: Green Bay PCB and Pesticide Values, 1993 - present (ng/m³)



Quality Assurance Parameters

Duplicate precision is reported for samples wherein detects were noted. Only 2 of the 3 planned duplicate samples were successfully collected. The first quarter duplicate was intended to be the spiked sample discussed below. Out of a total of 20 data pairs, there were no bad pairs, 18 non-detect pairs (90.0%), and 2 detect pairs (10.0%). Both detect data pairs are shown in the table below.

Table 5: PCB and Pesticide Duplicates (ng/m³)

Parameter Name	Sample Date	Primary	Duplicate	Average	% Diff
AROCOR 1242	07-Sep-97	0.19	0.18	0.19	5.4%
ATRAZINE	05-Jun-98	0.29	0.21	0.25	32.0%

A total of 3 blank samples had results returned during the 1997/1998 sampling season. No parameters were detected in any of these samples.

Spike recovery is a quality control technique whereby a known amount of a parameter of interest is introduced to sampling materials, which are then treated as a regular blank and a duplicate sample. This determination allows for a blind determination of sampling and analytical proficiency. An attempt at this failed through a combination of local herbicide use leading to potential contamination, and loss of spiked material through condensation away from the sampling material. There was not an opportunity during this sampling season to repeat the determination.

Inter Site Comparison

The sample schedules are coordinated between Green Bay and Wisconsin Rapids, so that sampling on the same day is intended. Sampler malfunctions and some operator errors or miscommunications have led to a number of samples that were not collected concurrently. Out of a total of 21 ambient samples collected at each site, 18 (85.7%) were collected during the same period.

The table below documents each of the sample sets collected during the same period, showing results (in ng/m³), whether PCBs were detected in the sample or not, the difference between them (Green Bay minus Wisconsin Rapids), and the percent difference relative to the Rapids value. Non-detects are evaluated at the detection limit, providing maximum possible concentrations.

Note that in all but one case, Green Bay values are higher, and that many more non-detects were recorded in Wisconsin Rapids. Overall, PCB concentrations observed in Green Bay average about twice those obtained during the same periods in Wisconsin Rapids, even when non-detects are evaluated at their maximum possible concentrations.

A t-test performed on this data set reveals these differences to be statistically significant to greater than 99% confidence limits. ($t = 3.626$, probability = 0.002) These results may

be indicative of the effect known sediment contamination can have on the local ambient air quality.

Table 6: Green Bay and Wisconsin Rapids PCB Comparison Data

Date	G.B.	Detected	W.R.	Detected	Difference	% Difference
09-Jul-97	0.30	Y	0.22	Y	0.08	34.9%
21-Jul-97	0.71	Y	0.19	Y	0.52	278.5%
14-Aug-97	0.26	Y	0.19	Y	0.07	34.9%
26-Aug-97	0.26	Y	0.24	Y	0.02	7.5%
09-Sep-97	0.35	Y	0.21	Y	0.14	69.2%
19-Sep-97	0.28	Y	0.12	Y	0.16	139.7%
13-Oct-97	0.19	Y	0.09	N	0.10	106.4%
06-Nov-97	0.13	Y	0.09	N	0.04	42.3%
30-Nov-97	0.05	N	0.07	Y	-0.02	-30.0%
24-Dec-97	0.05	Y	0.04	N	0.01	24.8%
17-Jan-98	0.04	Y	0.04	N	0.00	10.3%
10-Feb-98	0.09	Y	0.05	Y	0.04	84.3%
17-Mar-98	0.14	Y	0.05	Y	0.09	162.9%
23-Apr-98	0.26	Y	0.11	N	0.15	135.8%
05-May-98	0.45	Y	0.09	Y	0.36	407.1%
19-May-98	0.17	Y	0.10	Y	0.07	70.0%
05-Jun-98	0.15	Y	0.09	N	0.06	64.1%
16-Jun-98	0.31	Y	0.11	Y	0.20	181.8%
Average	0.23	17	0.12	12	0.12	99.5%

Comparisons between atrazine results are documented below. The four detects from Wisconsin Rapids correspond with 3 Green Bay detects and one non-detect. The table shows results (in ng/m³), whether atrazine was detected in the sample or not, the difference between sites (Green Bay minus Wisconsin Rapids), and the percent difference relative to the Rapids value. The non-detect is evaluated at the detection limit, providing maximum possible concentrations.

Note that each site has the higher value in half of the samples, and that the averages are essentially identical. A t-test performed on this data indicates that the sites are indistinguishable with respect to atrazine ($t = 0.252$, probability = 0.817). This herbicide is in current use in both central and northeastern Wisconsin. The variation between samples may reflect different application patterns between the two areas.

Table 7: Site Atrazine Comparison

Date	GB	Detected	WR	Detected	Difference	% Difference
05-May-98	0.20	N	0.25	Y	-0.05	-21.4%
19-May-98	0.65	Y	0.84	Y	-0.19	-22.6%
05-Jun-98	0.34	Y	0.24	Y	0.11	45.3%
16-Jun-98	0.47	Y	0.40	Y	0.07	17.5%
Average	0.42	3	0.43	4	-0.02	-3.9%

Green Bay PCB and Pesticide Trend Analysis

PCBs have been detected regularly since the 1993/1994 sampling season in Green Bay. Method improvements have resulted in a nearly 100% detection rate since May 1995. This quantity of data is sufficient for initial trend analysis. Data from two different sites is included in this analysis, requiring determination of whether the sites are observably different. Three sets of concurrent samples were obtained in May and June 1997 to investigate potential site differences.

Results from these samples are documented in the table below. Qualitatively, both PCB and atrazine values at the Fox River site are slightly higher, although most PCB and all atrazine results are within historic co-located duplicate samples differences. The former Fox River site was right on the river bank, and located near a property that was formerly used for repair of electrical equipment. This site may represent a local hot spot for PCBs.

A T test conducted on the data shows that the sites can not reliably be distinguished for both PCBs and atrazine ($t = 0.896$, probability = 0.465 for PCBs; $t = 2.642$, probability = 0.118 for Atrazine). Although it is possible that a larger number of samples would have revealed a significant difference between the sites, all Green Bay data is considered a single data set for further trend analysis on the basis of these results.

Table 8: Inter Site PCB Comparisons

Parameter Name	Sample Date	Fox River	Younkers	Average	% Diff	Detects
TOTAL PCBs	5/10/97	0.25	0.19	0.22	28.4%	Y/Y
TOTAL PCBs	5/24/97	0.65	0.44	0.54	38.5%	Y/Y
TOTAL PCBs	6/3/97	0.59	0.65	0.62	10.7%	Y/Y
Average		0.50	0.43		15.2%	
ATRAZINE	5/10/97	0.27	0.25	0.26	7.4%	Y/Y
ATRAZINE	5/24/97	0.23	0.22	0.22	4.5%	Y/Y
ATRAZINE	6/3/97	0.33	0.29	0.31	12.9%	Y/Y
Average		0.28	0.25		8.8%	

PCB data from Green Bay subjected to trend analysis is summarized in the following tables. The first table presents all data, with non-detects evaluated at the detection limit. Averages, maxima, minima and percent relative standard deviation are shown, along with the total number of detects and samples for each project year. The second table evaluates only the detected samples. It should be noted that the project year extends from July through June, and is numbered according to the calendar year in which it ends.

A major gap is present in our data. No samples were successfully collected between October 1993 and December 1994. A combination of sampling material supply problems, equipment malfunctions and operator errors led to this situation. Sample collection since December 1994 has been essentially continuous.

Table 9: Green Bay Yearly PCB Results, July 1993 - June 1998

Project Year	Average	Maximum	Minimum	%RSD	Detects	Samples	Detection Rate
Overall	0.40	2.15	0.04	79.7%	97	114	85.1%
1994	0.77	1.11	0.49	32.0%	6	7	85.7%
1995	0.36	0.80	0.20	50.7%	7	17	41.2%
1996	0.47	2.15	0.04	94.0%	25	27	92.6%
1997	0.39	1.30	0.04	78.1%	31	34	91.2%
1998	0.24	0.71	0.04	64.8%	20	21	95.2%

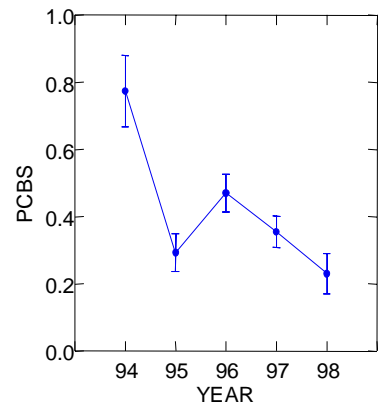
Table 10: Green Bay Yearly PCB Results, Detects Only

Project Year	Average	Maximum	Minimum	%RSD	Detects
Overall	0.44	2.15	0.04	77.8%	89
1994	0.76	1.11	0.49	35.2%	6
1995	0.52	0.80	0.28	33.8%	7
1996	0.50	2.15	0.04	90.6%	25
1997	0.42	1.30	0.04	71.3%	31
1998	0.25	0.71	0.04	61.4%	20

Application of ANOVA to both the complete and truncated data sets yields statistically significant differences in both the yearly and seasonal variations. Significant values obtained from the yearly statistical analyses are included in the table below. With the exception of 1995 (for which a significant portion of the data is missing), a nearly linear decreasing trend is observed. This is shown in the least squares means plot below.

Table 11: Significant Values from Yearly Statistical Analysis

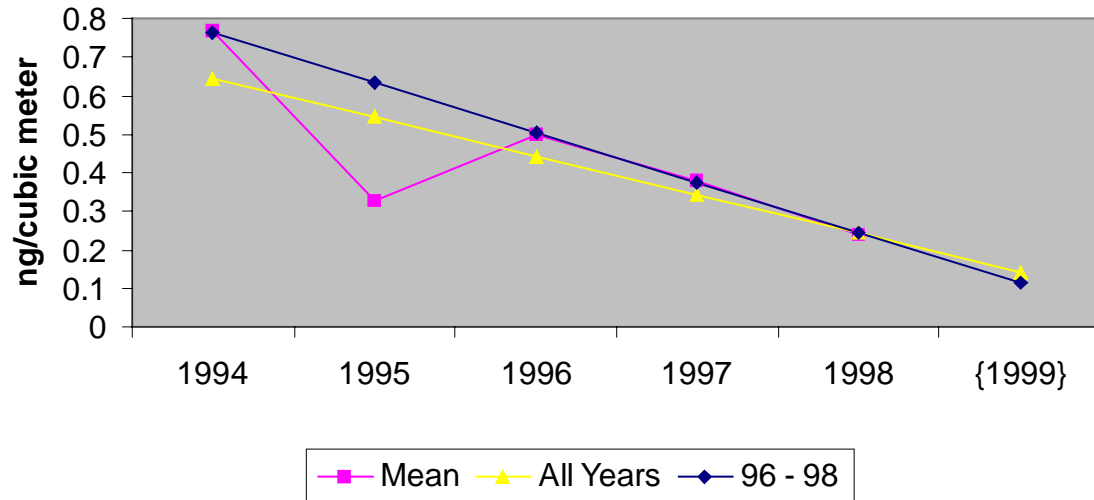
Yearly	F-ratio =	6.305	P =	0.000
All Values	95	96	97	98
94	0.000	0.013	0.000	0.000
95		0.027		
96				0.004
Detects Only	F-ratio =	4.806	P =	0.001
94	0.026		0.037	0.002
96				0.045

Figure 3: Yearly

Evaluation of the linearity observed with the yearly data was estimated using the least squares means (y-axis) versus the year (x-axis). When all years are incorporated, the regression coefficient (r^2) is 0.606 for the detects-only dataset, and 0.570 for the entire dataset. Incorporating only the data from 1996 on, the r^2 becomes 0.997 and 0.999, respectively. The graph below displays observed least squares means and trend lines calculated using the regressions mentioned above.

These results are highly indicative of a valid decreasing trend in ambient PCB concentrations. However, it should be noted that the 1994 and 1995 datasets are not complete, and that the clarity and magnitude of the trend may be exaggerated because of this.

Figure 4: PCB Trend, Observed and Calculated from Regression



Seasonal analysis is based on 3-month periods beginning in December (winter) being associated with each season. ANOVA testing of the data grouped in this manner yields highly significant differences between the seasons ($F = 19.478$ (all samples); 15.108 (detects only) $\text{prob} = 0.000$). Summer values are significantly higher than those of all other seasons, while fall and spring values are about equal and winter values are lowest. This trend is displayed in the following graph.

The data from Wisconsin Rapids also displays this seasonal trend, although at a slightly lower confidence level ($F = 8.198$, probability = 0.001). Figure 5 below shows the seasonal variation in Wisconsin Rapids. These observed trends are supported by the basic physical chemistry of semi-volatile organic compounds, which demonstrates a strong effect of temperature on vapor pressure, and therefore ambient air concentrations.

Figure 5: Seasonal PCB Variation in Green Bay

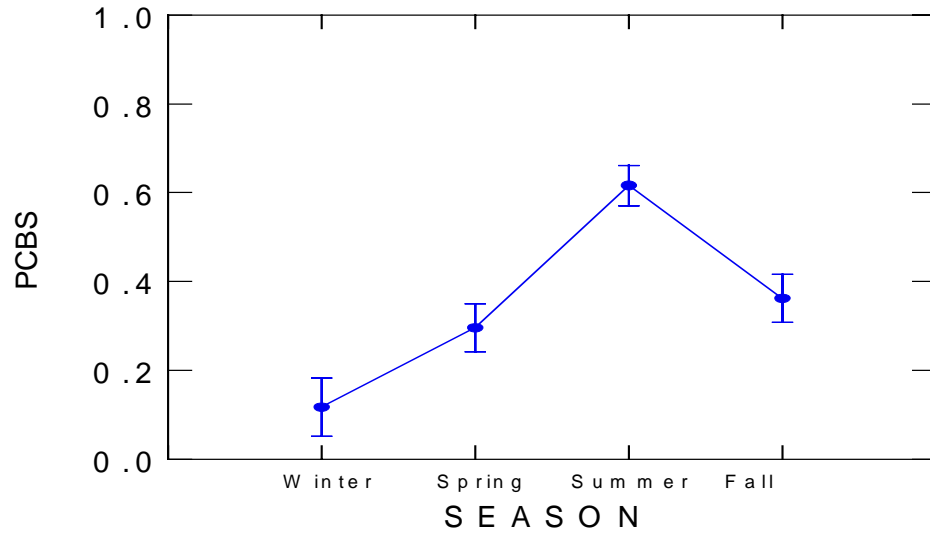
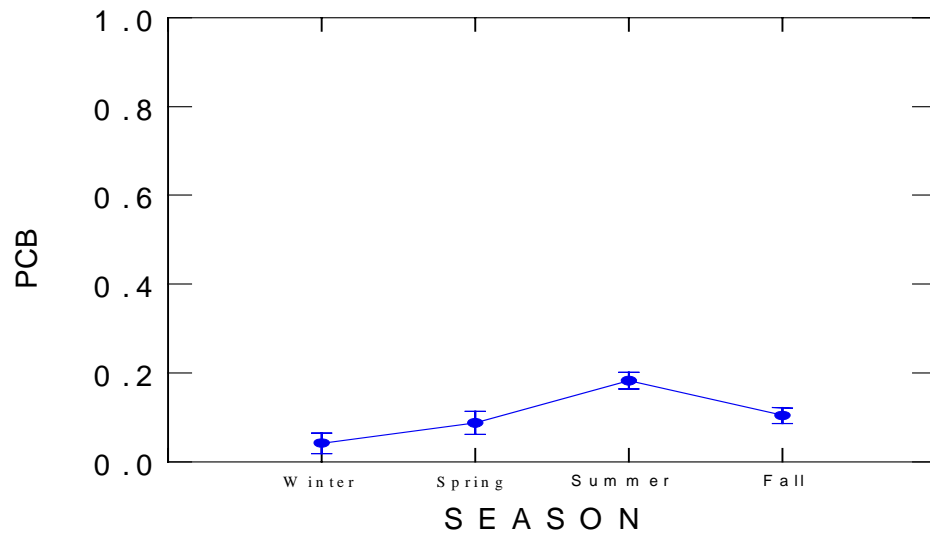


Figure 6: Seasonal PCB Variation in Wisconsin Rapids



PCB and Pesticide Parameter Conclusions

Analysis of the semi-volatile organic compound results yields the following pertinent points of interest:

- 1.** PCBs are present in low concentrations at all sites tested for this parameter to date. Results average about twice as high in Green Bay as Wisconsin Rapids based on the data through June 1998.
- 2.** A strong seasonal PCB trend is present in the data, with summer values statistically higher than those of all other seasons at all sites. Spring and fall values are higher than those obtained in winter. This trend is consistent with general physical properties of semi-volatile compounds.
- 3.** A decreasing trend is present with the Green Bay data. At this point it appears nearly linear. Further results will help clarify this.
- 4.** Atrazine is detected at all sites several times a year. Detects appear to correlate well with agricultural use.
- 5.** The other pesticide parameters incorporated into this study have only rarely been detected. Most of these parameters are no longer in current use, and removing them from the parameter list is advisable.

Non-Volatile Metal Parameters

Overview

All metals results and the associated total suspended particulate (TSP) data collected during WUATM sampling state wide are presented. Samples were collected in Superior, Milwaukee, Waukesha, Wisconsin Rapids and at the Trout Lake remote background site. In addition to the regular samples, three archived samples from Manitowoc and 2 samples from an additional site in Wisconsin Rapids were analyzed for metal parameters.

Background information on the uses, atmospheric sources and reported emissions in Wisconsin are included along with the basic data collected as part of WUATM. Nickel and manganese are included in the background information to help provide a basis for determining whether to incorporate these parameters into the WUATM metals program.

Parameter Uses and Atmospheric Sources

Arsenic, cadmium, chromium, lead, selenium and vanadium are the current metal parameters of interest in the WUATM program. All of these elements have potential natural sources, such as volcanic eruptions (which are capable of dispersing particles world-wide), forest fires and wind entrainment of mineral bearing soils. Each of the elements also has significant anthropogenic sources, including the manufacture, use and disposal of products containing them, combustion processes and development pressures increasing the prevalence of erosion and wild fires. In general, the fate of these elements is wind dispersal and subsequent wet or dry deposition.

Arsenic is used primarily as a wood preservative and in agricultural chemicals (insecticides, herbicides, algacides, and growth stimulants). These uses accounted for about 93% of the total consumption in the United States around 1990. Smaller amounts were also used in the production of glass and nonferrous alloys, and in the electronics industry. Releases of arsenic to the atmosphere can come from production of any of the above materials, combustion of coal or treated lumber, and use of arsenic containing chemicals. Primary atmospheric sources in Wisconsin are fossil fuel combustion related.

Cadmium is a heavy metal which is used mainly in batteries, pigments, metal coatings, plastics and alloys. One compound (cadmium sulfide) has been used in the conversion of solar energy to electrical power. Some cadmium compounds are used as fungicides for golf courses and home lawns. Metal production, industrial applications, manufacture of phosphate fertilizers, and coal, wood, and oil combustion are major contributors of cadmium to the atmosphere. Principal cadmium sources in Wisconsin include fossil fuel combustion, waste incineration and metals processing.

Chromium's fundamental uses are in the metallurgical, refractory and chemical industries. It is used to produce stainless steels and various alloys, with typical materials ranging from 11.5% to 30% chromium by weight. Chromium bearing materials have a strong heat resistance, and find use as linings for high temperature industrial furnaces.

Other uses include pigments, metal finishing, leather tanning, catalysts and wood preservatives.

Primary emission sources include the metal industries and fossil fuel combustion, accounting for about 45% and 26% to 45% of the total. A wide variety of minor sources are associated with the various uses and disposal of chromium bearing products. Principal atmospheric sources in Wisconsin include fuel combustion and metals processing.

Lead is a metal which has been widely used and dispersed into the environment since at least ancient Roman times. Recent uses with major environmental consequences that have been discontinued include gasoline additives and paint pigments. These uses have left a legacy of increased lead content in roadside dusts and in older houses. About 80% of lead used during 1990 was in lead-acid storage batteries.

Estimates of emissions on a national level indicate that between 1992 and 1995, industrial processes were responsible for about 60% of total emissions, with metals processing, recycling and waste incineration accounting for the majority of this. Transportation and combustion processes were responsible for about 25% and 10% , respectively, of the total estimated emissions.

The only metal more abundant in the earth's crust than manganese is iron. This common element does not occur as a free metal, but only as a component of minerals. Some uses of manganese and its compounds include steel production, dry cell batteries, matches and fireworks, catalyst applications, fertilizer and as an oxidizing agent. Primary atmospheric sources include industrial emissions, fossil fuel combustion and reentrainment of soils.

A significant potential source of manganese is the use of MMT (methylcyclopentadienyl manganese tricarbonyl) as a fuel additive. This compound was banned for this use in 1977, but a court order in 1995 rescinded the ban. Testing for health effects of this compound are ongoing. It has been estimated that if all gasoline contained MMT, ambient urban manganese levels would increase by about 50 ng/M³. The potential increase in MMT use is one of the prime motivating factors for considering addition of this element to the WUATM parameter list.

Nickel is the earth's third most abundant heavy metal. Most of this element is found within the mantle and core, where it is estimated to comprise 0.22% and 5.8%, respectively. Concentration in the crust ranges from <0.0001% - >0.3%. The primary use of nickel is metallurgical applications, where its presence in alloys imparts corrosion resistance, hardness and strength.

Other significant uses of nickel include alkaline batteries and catalytic applications. Natural sources, primarily windblown soil and volcanic eruptions, are estimated to contribute 15 - 20% of the total estimated yearly emissions. Major anthropogenic sources include fuel oil combustion, nickel processing industries, and municipal waste

incineration.

Selenium compounds are common and can be found in most rocks and soils. Selenium in the elemental form is rare, however, being obtained primarily as a byproduct of copper smelting. The element's photoelectric and semi-conductor properties make it useful for a wide variety of photo and xerographic applications. These uses accounted for almost half of the total processed in 1983. The glass industry consumes a significant quantity of selenium for tinting glass, and with other pigmentation applications accounts for another 40% of the annual demand for these compounds. A variety of uses including catalysts, and medical and nutritional preparations account for the remaining 10 - 15% .

The major source of anthropogenic Selenium in the atmosphere is combustion of coal and other fossil fuels. Estimates of the quantity of releases from these sources vary between about 1,000 and 2,000 tons per year nationwide. Additional sources include industrial and municipal waste incineration, along with primary production and processing of selenium containing materials. Natural sources of selenium to the atmosphere include microbial and plant action which converts the element to volatile compounds, and volcanic gases. The magnitude of these sources is not known, although some estimates of the releases rivals that of the anthropogenic sources. Principal selenium sources in Wisconsin are fossil fuel combustion related.

Vanadium is present throughout the earth's crust at an average concentration of 150 mg/kg (150 ppm by weight). Its uses are primarily in metallurgical applications, including alloying in steel, ferrovanadium alloys, and nonferrous titanium alloys. Minor uses include industrial catalyst applications, driers in paints and varnishes and as components in photographic developers. Atmospheric sources of this element include combustion of fossil fuels, especially fuel oils, and primary production of vanadium containing materials. Natural sources include continental dust, marine aerosol and volcanic eruptions. Few sources in Wisconsin report this parameter. Most of them are fossil fuel combustion related.

Reported Emissions

Industrial sources which emit quantities of toxic materials above particular limits are required to report their emissions to the DNR. Reporting requirements have varied over the years, both in reporting limits and targeted compounds. In addition, recognition of all sources which should be reporting may not be complete. As such, it is important to note that the data in the tables below should be used only as a rough guideline for total emissions of these metals.

Statewide reported toxic releases for each of the parameters between 1993 and 1997 are summarized in the tables below. The first table lists the number of reporting sources and emissions by parameter. It should be noted that copper and iron emissions are reported

in significant quantity also. The second table summarizes these emissions by the size of the source (greater than 1000 pounds per year and greater than 100 pounds per year). This table has been included to illustrate that a relatively few sources are responsible for the majority of reported metals emissions in the state.

Table 12: Reported Industrial Emissions of Study Metals in Wisconsin

Hazardous Air Pollutant	Data	1997	1996	1995	1994	1993
Total Arsenic as As	Sources	73	71	68	87	82
	Emissions	4975.3	4789.0	4202.0	7490.1	14826.5
	Percent of Emissions	2.8%	2.8%	2.4%	4.4%	7.7%
Total Cadmium as Cd	Sources	73	73	67	81	74
	Emissions	2700.0	2621.1	1855.7	1719.1	1861.8
	Percent of Emissions	1.5%	1.5%	1.0%	1.0%	1.0%
Total Chromium, as Cr	Sources	102	87	84	105	110
	Emissions	19989.3	25306.7	23649.2	24671.4	20379.8
	Percent of Emissions	11.3%	14.6%	13.3%	14.4%	10.5%
Total Lead, as Pb	Sources	33	25	23	15	17
	Emissions	50777.3	49969.5	68789.5	48431.6	39804.9
	Percent of Emissions	28.8%	28.9%	38.6%	28.2%	20.6%
Total Manganese, as Mn	Sources	76	74	76	99	101
	Emissions	64320.7	57278.0	54333.1	62988.9	71921.3
	Percent of Emissions	36.4%	33.1%	30.5%	36.7%	37.2%
Total Nickel, as Ni	Sources	88	85	86	113	120
	Emissions	23222.0	23787.6	16092.6	21782.8	29414.2
	Percent of Emissions	13.1%	13.8%	9.0%	12.7%	15.2%
Total Selenium, as Se	Sources	38	32	32	44	34
	Emissions	8695.2	7561.9	7719.0	2847.6	8890.0
	Percent of Emissions	4.9%	4.4%	4.3%	1.7%	4.6%
Total Vanadium, as V₂O₅	Sources	5	3	2	4	11
	Emissions	1926.4	1600.3	1427.8	1858.4	6421.0
	Percent of Emissions	1.1%	0.9%	0.8%	1.1%	3.3%
Parameter Sources		488	450	438	548	549
Parameter Emissions		176606.4	172914.1	178068.9	171789.9	193519.4
Percent of All Reported Parameters		66.5%	69.5%	61.4%	51.6%	47.3%
All Metal Reporting Sources		743	698	679	827	828
All Reported Metal Emissions		265719.8	248885.8	290152.8	332856.0	409181.0
Total Percent of Emissions		100.0%	100.0%	100.0%	100.0%	100.0%

Table 13: Major Source Contributions to Reported Wisconsin Metal Emissions

Year	1997	1996	1995	1994	1993
Highest Single Source	29170.0	27358.4	33914.0	36733.0	31565.0
Percent of Total	16.5%	15.8%	19.0%	21.4%	16.3%
Sources > 1000 lbs					
Count of Sources	37	35	26	36	42
Sum of Emissions	132652.8	127525.3	131130.4	124546.9	144054.0
Percent of Sources	7.6%	7.8%	5.9%	6.6%	7.7%
Percent of Emissions	75.1%	73.8%	73.6%	72.5%	74.4%
Sources > 100 lbs					

Count of Sources	158	158	156	157	177
Sum of Emissions	172612.4	169292.1	174636.7	165791.7	187182.9
Percent of Sources	32.4%	35.1%	35.6%	28.6%	32.2%
Percent of Emissions	97.7%	97.9%	98.1%	96.5%	96.7%

The next tables summarize metal emissions on a county basis. The first shows Wood county emissions by parameter, while the second summarizes total metal emissions from counties which report greater than 10,000 pounds per year on a consistent basis. The final table documents reporting limits for the parameters of interest.

Table 14: Reported Wood County Emissions (lb/yr)

Hazardous Air Pollutant	1997	1996	1995	1994	1993
Total Arsenic as As	151.7	265.5	253.6	111.6	686.1
Total Cadmium as Cd	43.9	31.1	34.0	41.0	8.6
Total Chromium as Cr	72.8				0.6
Total Manganese as Mn	3015.1	2228.1	419.0	1.7	8191.4
Total Nickel as Ni	1332.0	1115.4	1205.5	809.2	4639.4
Total Selenium as Se	0.1			75.0	31.9
Grand Total	4615.6	3639.9	1912.1	1038.5	13558.0
Percent of Total	2.6%	2.1%	1.1%	0.6%	7.0%

Table 15: Emissions by Counties Reporting >10,000 Pounds per Year

County	1997	1996	1995	1994	1993
GREEN	10424	14760	8736	10996	NR
% Total	5.9%	8.5%	4.9%	6.4%	0.0%
MANITOWOC	26349	23816	NR	2422	1442
% Total	14.9%	13.8%	0.0%	1.4%	0.7%
MILWAUKEE	15053	16700	34162	12375	11098
% Total	8.5%	9.7%	19.2%	7.2%	5.7%
OUTAGAMIE	9486	11248	10183	10712	12977
% Total	5.4%	6.5%	5.7%	6.2%	6.7%
SHEBOYGAN	35885	33850	42012	52063	52345
% Total	20.3%	19.6%	23.6%	30.3%	27.0%
WAUPACA	19203	15469	15116	9460	12488
% Total	10.9%	8.9%	8.5%	5.5%	6.5%

Table 16: Emission Reporting Limits (lb/yr)

Reporting Limits	Lb/Yr
Arsenic and inorganic compounds, as As	12
Cadmium and cadmium compounds, as Cd	12
Chromium (II) compounds, as Cr	179
Chromium (III) compounds, as Cr	179
Chromium (VI) compounds, as Cr, water soluble	18
Chromium (VI) compounds, as Cr, water insoluble	1
Chromium (metal)	179
Lead compounds	6000
Manganese Compounds	1114

Nickel Compounds other than Nickel Subsulfide	125
Nickel Subsulfide	12
Selenium and compounds, as Se	73
Vanadium, as V2O5, respirable dust and fumes	179

Current TSP and Metals Data Completeness

Samples are collected on a one in thirty day schedule. This low level of sampling tends to reduce the certainty of our average observations and increasing the standard error. With five sites, a total of 65 samples could have been analyzed. An evaluation of the representativeness of our current data set with the respect to site specific TSP data is discussed with the results.

Project completeness with reference to TSP and metals is documented in the following table. In this table, Completeness is the ratio of valid ambient samples that were analyzed for metals, to total sampling days. A total of 63 valid sets of metals analysis were obtained from the lab, for an overall completeness of 96.9%. Reasons for missing samples may include sampler failures, and field or laboratory miscommunications.

Table 17: Statewide Metals Completeness by Site

Site	Completeness	Valid	Samples	Void	Sampling Days
Wisconsin Rapids	92.3%	12	12	0	13
Superior	92.3%	12	12	0	13
Milwaukee	100.0%	13	13	0	13
Trout Lake	100.0%	13	13	0	13
Waukesha	100.0%	13	13	0	13
Total	96.9%	63	63	0	65

Analytical Results

Results for TSP and metals analysis for all sites are presented in the following tables. Values reported are in ug/M³ for TSP and ng/M³ for metal parameters. Averages, maxima, minima and %relative standard deviations are shown, along with the number of samples, the number of detects per parameter and the resulting % detection. Non-detects are valued at the detection limit in this section. This is the general convention used in the WUATM to generate maximum potential concentrations for the evaluation of health risks.

Table 18: Milwaukee Metal Results (ng/m³, except TSP in ug/m³)

Parameter	Average	Maximum	Minimum	RSD (%)	Detects	Samples	Detection Rate
ARSENIC	1.4	3.9	0.7	61.4%	13	13	100.0%
CADMIUM	0.6	1.5	0.2	70.5%	13	13	100.0%
CHROMIUM	7.2	36.1	2.3	122.7%	13	13	100.0%

LEAD	15.7	24.0	4.3	38.5%	13	13	100.0%
SELENIUM	1.0	1.9	0.2	52.1%	13	13	100.0%
VANADIUM	2.3	13.7	1.0	147.1%	7	13	53.8%
TSP	42	72	19	45.7%		13	

Table 19: Superior Metal Results (ng/m³, except TSP in ug/m³)

Parameter	Average	Maximum	Minimum	RSD (%)	Detects	Samples	Detection Rate
ARSENIC	1.0	2.4	0.6	49.8%	9	12	75.0%
CADMIUM	0.2	0.4	0.2	29.7%	12	12	100.0%
CHROMIUM	4.0	8.8	1.5	51.8%	12	12	100.0%
LEAD	8.9	19.6	1.0	63.5%	12	12	100.0%
SELENIUM	0.6	0.7	0.4	11.3%	2	12	16.7%
VANADIUM	3.3	11.6	0.7	107.6%	9	12	75.0%
TSP	54	148	10	75.9%		12	

Table 20: Trout Lake Metal Results (ng/m³, except TSP in ug/m³)

Parameter	Average	Maximum	Minimum	RSD (%)	Detects	Samples	Detection Rate
ARSENIC	0.6	0.9	0.1	28.9%	5	13	38.5%
CADMIUM	0.2	0.3	0.1	45.2%	13	13	100.0%
CHROMIUM	2.3	3.1	1.5	23.9%	13	13	100.0%
LEAD	1.9	3.8	0.1	49.8%	13	13	100.0%
SELENIUM	0.6	0.7	0.4	10.8%	3	13	23.1%
VANADIUM	1.0	1.3	0.6	14.5%	2	13	15.4%
TSP	11	27	2	78.5%		13	

Table 21: Waukesha Metal Results (ng/m³, except TSP in ug/m³)

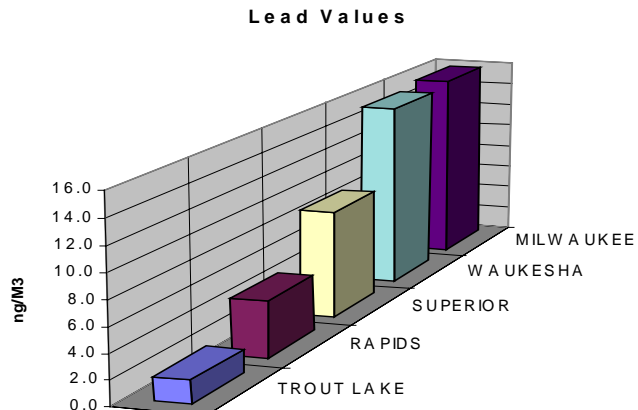
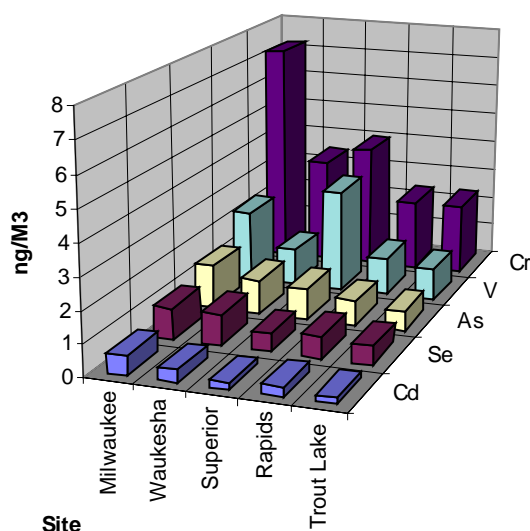
Parameter	Average	Maximum	Minimum	RSD (%)	Detects	Samples	Detection Rate
ARSENIC	1.1	3.4	0.5	70.6%	11	13	84.6%
CADMIUM	0.4	0.9	0.2	55.0%	13	13	100.0%
CHROMIUM	3.4	7.3	1.0	43.5%	12	13	92.3%
LEAD	15.4	45.9	4.5	84.4%	13	13	100.0%
SELENIUM	1.0	2.4	0.2	62.6%	9	13	69.2%
VANADIUM	1.2	2.5	0.4	43.2%	5	13	38.5%
TSP	40	71	16	43.6%		13	

Table 22: Wisconsin Rapids Metal Results (ng/m³, except TSP in ug/m³)

Parameter	Average	Maximum	Minimum	RSD (%)	Detects	Samples	Detection Rate
ARSENIC	0.8	1.8	0.4	44.9%	9	12	75.0%
CADMIUM	0.3	1.1	0.1	81.5%	12	12	100.0%
CHROMIUM	2.3	3.7	1.2	38.2%	12	12	100.0%
LEAD	4.6	8.7	1.4	54.1%	12	12	100.0%
SELENIUM	0.7	1.5	0.2	52.5%	4	12	33.3%
VANADIUM	1.2	2.1	1.0	33.8%	5	12	41.7%
TSP	23	39	11	43.2%		13	

The average values for each parameter except TSP are portrayed in the following graphs.

Figure 7: Statewide Metal Results, by site and parameter



Additional Metal Samples

Samples collected from 2 other TSP sites were analyzed for metals during the 1997/1998 sampling year. These include 3 samples from the City Hall site in Manitowoc (AIRS # 55-071-0001) and two samples from the 9th Avenue site in Wisconsin Rapids (AIRS # 55-141-0013). It is important to note that these samples do not fit within the usual scope of WUATM work.

General WUATM samples are intended to investigate typical contaminant concentrations one may be exposed to in urban air, rather than a particular source. Samples from the Manitowoc site, however, were chosen specifically to determine whether the impact of a major metal source located within a mile of the monitoring site could be measured. Wind direction was correlated with mid-range TSP loading on archived filters to evaluate which samples would best represent significant loading from this source.

The 9th Avenue site in Wisconsin Rapids is a source oriented neighborhood scale site established next to a small metal working plant. Two samples were submitted for metals analysis in the course of exceedence investigation. It is important to note that the local source in question is too small to be included in emission reporting requirements for these metals.

Table 23: Manitowoc Sample Results (ng/m³)

Parameter	Average	Maximum	Minimum	RSD (%)	Detects	Samples	Detection Rate
ARSENIC	2.1	3.5	1.3	60.1%	3	3	100.0%
CADMIUM	0.8	1.0	0.5	34.7%	3	3	100.0%

CHROMIUM	4.7	5.1	4.4	7.4%	3	3	100.0%
LEAD	27.6	39.6	21.6	37.7%	3	3	100.0%
SELENIUM	3.2	5.4	1.7	60.8%	3	3	100.0%
VANADIUM	8.1	10.3	7.0	23.5%	3	3	100.0%

Table 24: Wisconsin Rapids Sample Results (ng/m³)

Parameter	Average	Maximum	Minimum	RSD (%)	Detects	Samples	Detection Rate
ARSENIC	1.0	1.1	0.9	12.4%	2	2	100.0%
CADMIUM	0.2	0.3	0.2	12.3%	2	2	100.0%
CHROMIUM	7.2	8.8	5.6	32.1%	2	2	100.0%
LEAD	16.9	22.6	11.2	47.5%	2	2	100.0%
SELENIUM	0.6	0.6	0.6	8.5%	0	2	0.0%
VANADIUM	1.5	1.8	1.1	34.5%	1	2	50.0%

Site Intercomparison

Intercomparison of sites for this year's data is strictly qualitative. Statistical determination of differences between the results from the different sites has not been performed this year. Results from all three years of the statewide metals program will be compiled and evaluated thoroughly following the 1998/1999 sampling season.

Results for each parameter are grouped by site, and the average ratio to Trout Lake results shown in the following tables. Note that the 3 source oriented Manitowoc samples have the highest averages for all parameters except Chromium, and that the Rapids foundry results are high in Chromium and Lead. These results demonstrate the potential use of deploying samplers in areas expected to be subject to industrial impact.

The differences between the two Wisconsin Rapids sites (listed as Rapids Foundry and Witter Field in the table) are especially revealing, considering the sites are located within 2 miles of each other, and the industry affecting the 9th Avenue site is considered a minor source. It would be worthwhile to perform regular metals analysis on samples from these locations, to determine whether typical values are elevated over the other sites.

Table 25: Results Comparison (ng/m³)

ARSENIC	Average	Maximum	Minimum	RSD (%)	Detects	Samples	Detection Rate	Ratio: TL
MANITOWOC	2.1	3.5	1.3	60.1%	3	3	100.0%	3.4
MILWAUKEE	1.4	3.9	0.7	61.4%	13	13	100.0%	2.4
WAUKESHA	1.1	3.4	0.5	70.6%	11	13	84.6%	1.8
SUPERIOR	1.0	2.4	0.6	49.8%	9	12	75.0%	1.7
RAPIDS FOUNDRY	1.0	1.1	0.9	12.4%	2	2	100.0%	1.7
WITTER FIELD	0.8	1.8	0.4	44.9%	9	12	75.0%	1.3
TROUT LAKE	0.6	0.9	0.1	28.9%	5	13	38.5%	1.0
CADMIUM								
MANITOWOC	0.8	1.0	0.5	34.7%	3	3	100.0%	4.9
MILWAUKEE	0.6	1.5	0.2	70.5%	13	13	100.0%	3.6
WAUKESHA	0.4	0.9	0.2	55.0%	13	13	100.0%	2.6
WITTER FIELD	0.3	1.1	0.1	81.5%	12	12	100.0%	2.2
SUPERIOR	0.2	0.4	0.2	29.7%	12	12	100.0%	1.5
RAPIDS FOUNDRY	0.2	0.3	0.2	12.3%	2	2	100.0%	1.3
TROUT LAKE	0.2	0.3	0.1	45.2%	13	13	100.0%	1.0
CHROMIUM								
MILWAUKEE	7.2	36.1	2.3	122.7%	13	13	100.0%	3.1
RAPIDS FOUNDRY	7.2	8.8	5.6	32.1%	2	2	100.0%	3.2
MANITOWOC	4.7	5.1	4.4	7.4%	3	3	100.0%	2.1
SUPERIOR	4.0	8.8	1.5	51.8%	12	12	100.0%	1.7
WAUKESHA	3.4	7.3	1.0	43.5%	12	13	92.3%	1.5
WITTER FIELD	2.3	3.7	1.2	38.2%	12	12	100.0%	1.0
TROUT LAKE	2.3	3.1	1.5	23.9%	13	13	100.0%	1.0
LEAD								
MANITOWOC	27.6	39.6	21.6	37.7%	3	3	100.0%	14.8
RAPIDS FOUNDRY	16.9	22.6	11.2	47.5%	2	2	100.0%	9.0
MILWAUKEE	15.7	24.0	4.3	38.5%	13	13	100.0%	8.4
WAUKESHA	15.4	45.9	4.5	84.4%	13	13	100.0%	8.2
SUPERIOR	8.9	19.6	1.0	63.5%	12	12	100.0%	4.8
WITTER FIELD	4.6	8.7	1.4	54.1%	12	12	100.0%	2.4
TROUT LAKE	1.9	3.8	0.1	49.8%	13	13	100.0%	1.0
SELENIUM								
MANITOWOC	3.2	5.4	1.7	60.8%	3	3	100.0%	5.4
WAUKESHA	1.0	2.4	0.2	62.6%	9	13	69.2%	1.6
MILWAUKEE	1.0	1.9	0.2	52.1%	13	13	100.0%	1.7
WITTER FIELD	0.7	1.5	0.2	52.5%	4	12	33.3%	1.2
TROUT LAKE	0.6	0.7	0.4	10.8%	3	13	23.1%	1.0
SUPERIOR	0.6	0.7	0.4	11.3%	2	12	16.7%	1.0
RAPIDS FOUNDRY	0.6	0.6	0.6	8.5%	0	2	0.0%	1.0
VANADIUM								
MANITOWOC	8.1	10.3	7.0	23.5%	3	3	100.0%	8.2
SUPERIOR	3.3	11.6	0.7	107.6%	9	12	75.0%	3.4
MILWAUKEE	2.3	13.7	1.0	147.1%	7	13	53.8%	2.4
RAPIDS FOUNDRY	1.5	1.8	1.1	34.5%	1	2	50.0%	1.5
WAUKESHA	1.2	2.5	0.4	43.2%	5	13	38.5%	1.2
WITTER FIELD	1.2	2.1	1.0	33.8%	5	12	41.7%	1.2
TROUT LAKE	1.0	1.3	0.6	14.5%	2	13	15.4%	1.0

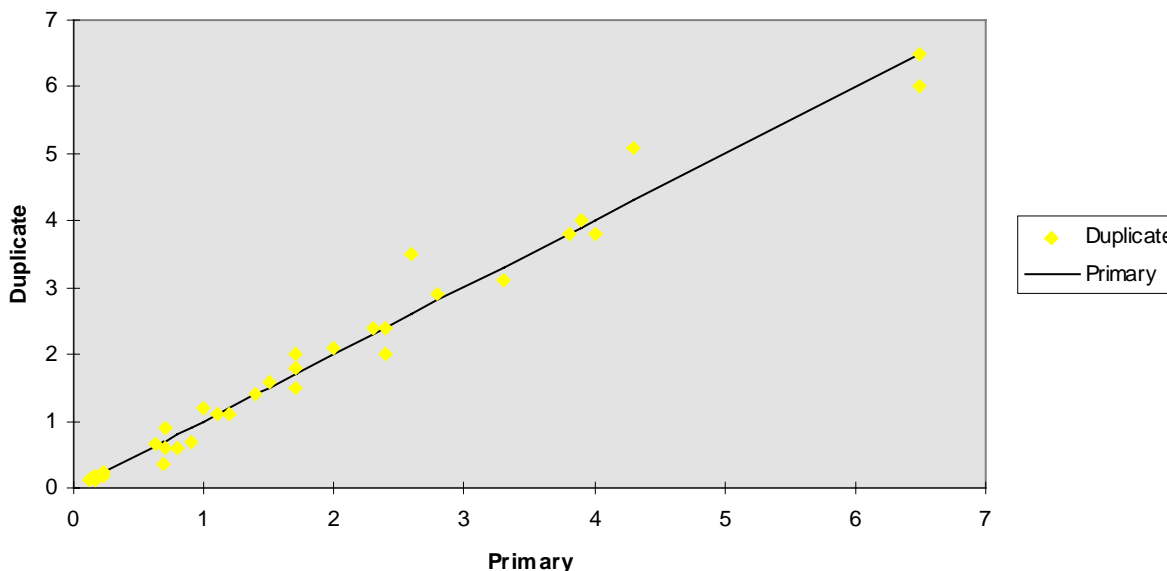
Quality Assurance Parameters

Quality assurance parameters reported by the laboratory include a total of eight filters analyzed in duplicate. Results from these samples are summarized below. There were no blank or split spiked samples reported this year. Please note that the data is in ug/Liter of solution. Common factors (dilution factor and sample volume) allow for the direct application of the percentage differences to general metals determinations.

Duplicate analysis show a total of 48 data pairs, of which 9 (18.8%) are non-detect pairs with qualitative agreement. A single pair, (2.1%) consists of one detect at the detection limit, while the duplicate analysis yields a non-detect. These values are considered qualitatively the same. A total of 2 pairs (4.2%) are classified as “bad pairs”, where one of the analyses showed a definitely detectable quantity, and the other didn’t. Of the remaining 36 (75.0%) detect pairs, 5 (10.4%) show a greater than $\pm 25\%$ difference. The overall average percent difference between duplicate analysis is 12.2%.

This value represents a slight improvement compared to the previously reported values, which were $\pm 14.3\%$ and $\pm 15.2\%$, respectively. The current duplicate values are well within the quality control target of $\pm 15.0\%$. Ambient concentrations presented are based on the reported values, without further reference to the $\pm 15\%$ built into the method. A comparison of primary and duplicate results is shown in the following graph. The two greatest data pairs (10.7/10.9 and 37.5/37.7 ug/L) have been left out of this graph to reduce the overall scale and improve clarity.

Figure 8: Comparison of Primary and Duplicate Analyses



Data Representativeness

A major concern is the representativeness of our data set, especially considering the low sampling frequency. The Milwaukee, Waukesha and Trout Lake sites collected samples on a one in six day or one in three day schedule. This allows a comparison of TSP results from the metals samples with the overall TSP results by site to provide a measure of representativeness.

The table below summarizes the pertinent TSP data by site. In all cases, the average \pm the standard deviation of the metal sample TSP results encompasses the average of the total TSP data set, implying that the smaller set adequately represents the mean of the total population. This implication is not as strong as the previous year's data, wherein the average \pm the standard error encompassed the full data set average.

The representativeness of the data is further examined through graphically representing the metals TSP subset alongside the overall TSP data in a box plot and in distribution graphs. In all of these representations, the data appears to show that the samples chosen for metals analysis are adequately representative of typical TSP samples collected from the sites.

Table 26: Statewide TSP Comparisons for Representativeness of Metals Sampling Protocol

Site	Average	Maximum	Minimum	Std Err	Std Dev	Samples
Milwaukee (metals)	42	72	19	5	19	13
Milwaukee	48	104	10	3	26	60
Trout Lake (metals)	11	27	2	2	8	13
Trout Lake	13	79	1	2	12	60
Waukesha (metals)	40	71	16	5	17	13
Waukesha	51	123	10	2	23	120

Figure 9: Box Plot Relating Site TSP Values to Site Metal Sample TSP Values

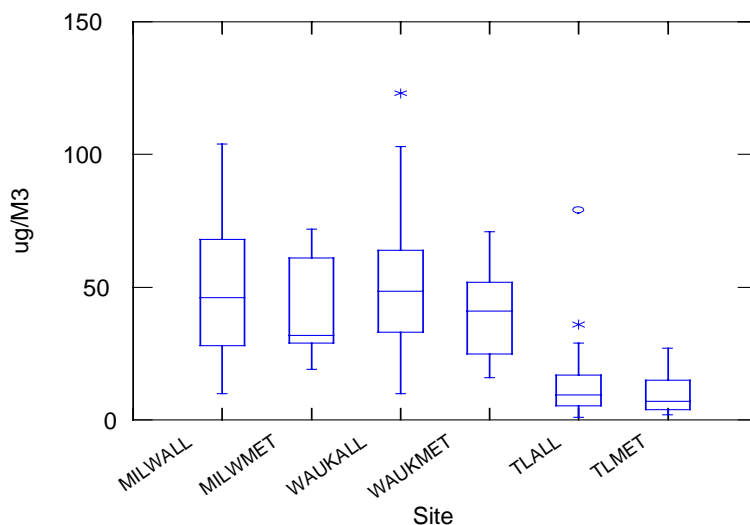
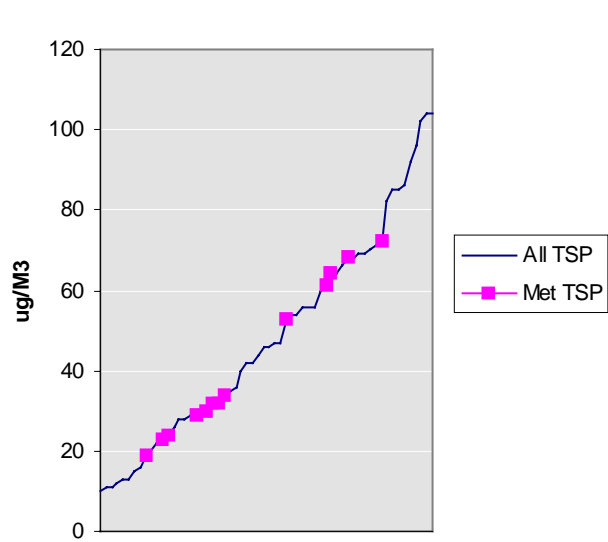
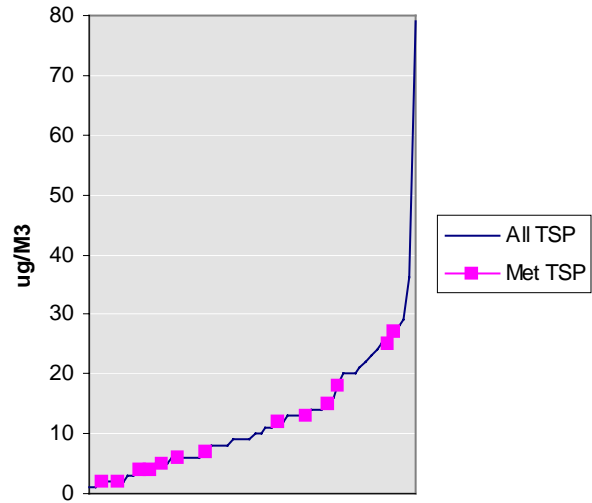


Figure 10: Distribution of Metals Samples Among TSP Samples

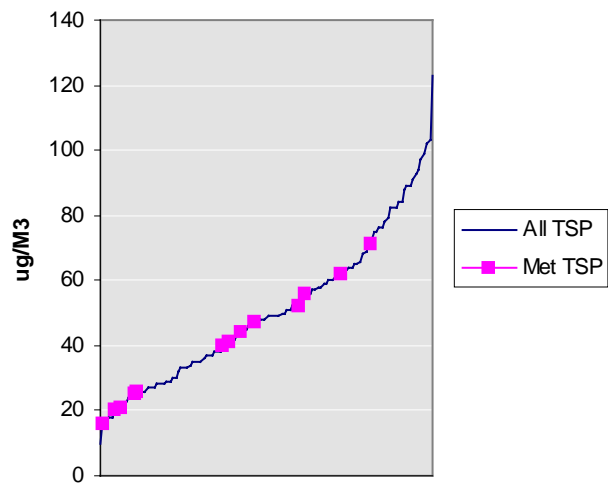
Milwaukee TSP Distribution



Trout Lake TSP Distribution



Waukesha TSP Distribution



Inorganic Parameter Conclusions

Qualitative analysis of the statewide metals sampling and analysis programs yields the following pertinent points of interest:

1. The statewide metals sampling program operates at a lowered confidence level because of the decrease in sampling frequency. Differences between the different sites chosen for the statewide program are observable in spite of the lowered confidence level.
2. Comparison of the urban sites to Trout Lake indicates the potential of determining urban impact with respect to these parameters. This potential will be investigated further in the future, as more data is collected.
3. Witter Field values are generally low, frequently near background levels obtained from Trout Lake. The pair of samples analyzed from the 9th Avenue site in Wisconsin Rapids are elevated in chromium and lead, and indicate the potential local impact of small neighborhood sources not required to report emissions.
4. Results from the Superior site are generally low (with the exception of Vanadium values), indicating that this site could readily be moved to another location.
5. Selenium and vanadium results continue to show a significant percentage of non-detects, indicating that dropping these parameters in favor of other potential parameters of interest is advisable.
6. Although emission reporting may not be a valid indicator of actual emissions, this resource may provide important information for determining potential site locations and parameter choices.
7. Emissions inventories indicate that Sheboygan, Manitowoc and Waupaca counties generally report the highest metal emissions.
8. Results of metal analysis from the former City Hall site in Manitowoc appear to support the emission inventory, showing elevated levels of most parameters.

Carbonyl Parameters

Overview

The primary carbonyl parameter in the WUATM study is formaldehyde, with some data present for acetaldehyde, acetone and occasional detects of acrolein and others. Consistent data on parameters other than formaldehyde has not been obtained. All July 1997 - June 1998 WUATM and 24 hour PAMS carbonyl data is presented in this report.

Samples were collected from the Witter Field site in Wisconsin Rapids and from the UW North PAMS site. Additional samples have been collected on a 3 hour basis at UWM and two additional sites along Lake Michigan (Harrington Beach State Park and Manitowoc). These results are not included as they are not directly comparable to the existing WUATM data set.

Background information on the uses, atmospheric sources and reported emissions of acetaldehyde, acrolein and formaldehyde in Wisconsin are included along with the data. The previous report (AM294-99) summarizes historic UWM and Green Bay formaldehyde results including seasonal and yearly trend analysis, and inter-site comparisons. This report documents current data, with qualitative comparison between the current Milwaukee and Wisconsin Rapids sites, and the historic formaldehyde data.

Parameter Uses and Atmospheric Sources

This organic parameter group is named after the reactive functional group which characterizes it. A carbonyl functional group contains a carbon double bonded to an oxygen (written as C=O), with the other 2 carbon bonding sites occupied by hydrogen atoms or other carbon groups. The carbonyl group is relatively unstable and subject to reacting easily.

This property causes compounds in this class to have short atmospheric lifetimes. However, photochemical degradation of general hydrocarbons (both natural and anthropogenic) tends to form these compounds, thus providing indirect sources to maintain their presence in ambient air. The reactivity of this class of compound has led to their inclusion as part of the Enhanced Ozone Monitoring program, while their ubiquitous presence and toxicity merits the attention of the WUATM program.

Formaldehyde is a highly reactive, colorless organic gas with a pungent odor. It is widely present in the atmosphere at low concentrations, through both myriad consumer and industrial uses, and as a product of incomplete combustion. Indirect production through photochemical oxidation of hydrocarbons released from combustion processes may be greater than direct production at times.

Natural mechanisms for formaldehyde removal include dissolution in water, where it breaks down readily through biological processes, direct photolysis and oxidation by photo-chemically produced species in the air. The compound is very short lived, with some half-life estimates ranging from 1.6 to 19 hours, dependent upon atmospheric

conditions.

Complete oxidation of formaldehyde yields carbon dioxide and water, however it tends to form intermediates known as free radicals, which participate in further atmospheric reactions. The compound has been implicated in the ozone formation and degradation cycles, and is included in the PAMS monitoring program for this reason.

Uses of formaldehyde include being an intermediate in the industrial production of organic chemicals; production of urea-formaldehyde resins which are used in plywood glues; particle board products and insulating foams; disinfecting and preservative products; slow release fertilizers; and as an anti-bacterial agent in many cosmetic and disinfectant products.

The wide variety of consumer product uses and volatile nature of the material lead to a situation where it is common for indoor concentrations of formaldehyde to be much greater than those typically found outdoors. This is especially true in newer and mobile homes, where out-gassing from construction materials is typical. As the materials age, out-gassing decreases, and concentrations gradually lower.

Emissions of biogenic compounds from natural sources also fuel the formation of atmospheric formaldehyde, through essentially the same reaction pathways that products of incomplete combustion follow. Elevated concentrations in remote sites are frequently associated with long range transport of reactive organic compounds, rather than local, direct sources of formaldehyde.

Acrolein is reactive volatile organic compound with a disagreeable odor. In the vapor phase it reacts rapidly with other atmospheric components to form carbon monoxide, formaldehyde, nitric acid and other products. Its primary uses include chemical synthesis of a variety of compounds, and biocide applications in irrigation waters, cooling waters, paper processes and oil wells.

Potential sources of acrolein include emissions from the use of acrolein (the greatest reported releases in Wisconsin are related to the paper industry), secondary formation in atmospheric reactions of hydrocarbon pollutants, and combustion of fossil fuels and plant materials. It is also produced by heating fats, oils and plastics.

Acetaldehyde is a gas at room temperature and has a pungent, fruity odor. It is highly reactive and has a short residence time in the atmosphere. Its primary uses include synthesis of a wide range of chemicals, silvering mirrors and in synthetic flavoring agents. Along with ethanol, it is the primary VOC component of natural fermentation emissions.

Potential sources of acetaldehyde include emissions from the use of it, fermentation emissions, paper processing and incomplete combustion. The primary reporting sources in Wisconsin are related to the paper industry, yeast production and baking processes.

Reported Emissions

Industrial sources which emit quantities of toxic materials above particular limits are required to report their emissions to the DNR. Reporting requirements have varied, and all potential sources may not be identified. The reported emissions are typically estimated based on process material throughput and standard emission factors which have been developed by the EPA. Significant variation among facilities operating similar equipment is common, and may not be reflected in the standard emission factors.

These factors render reported emissions data useful mostly as an order of magnitude estimate of industrial emissions. The significant quantities of carbonyl compounds emitted from non-industrial sources and formed in atmospheric reactions from anthropogenic pre-cursors are difficult to assess. As such, emissions reported in the following tables must be regarded as a very rough guideline, rather than a true estimate of Wisconsin's atmospheric carbonyl compound inputs.

Reported toxic releases both statewide, and in selected counties, between 1990 and 1997 are summarized in the table below. Emissions are in pounds per year. Two formaldehyde values from the original AEMS data have been altered. One source reported over 12,000,000 pounds emitted in 1992, while all other years reported are around 400. This value was deleted. Another source reported over 3,000,000 pounds emitted in 1991, while all other years on record are less than 1/10th that level and decreasing. This value was divided by 10.

It should be noted that in general emissions appear to be decreasing since the advent of reporting in response to the Clean Air Act in 1990. Many major sources have improved either their pollution control, or their emission estimation assumptions, to reduce their annual output of this pollutant. Combustion processes are a major source that can be minimized by better monitoring and control of boiler conditions. More efficient combustion implies lessened energy cost, which may help spur efforts to decrease atmospheric inputs.

It is also interesting to note that a significant number of sources report estimated emissions of less than a pound per year. This represents a value less than the average amount associated with an individual's personal production of formaldehyde and acetaldehyde related to use of gas fired appliances, personal vehicles and smoking.

The minimum required reporting limit for formaldehyde is 125 pounds per year. Acetaldehyde reporting limits are 6000 pounds per year, while acrolein reporting is required above 91 pounds per year.

Table 27: Reported Industrial Emissions of Carbonyl Compounds in Wisconsin,

HAP	Data	1990	1991	1992	1993	1994	1995	1996	1997
Acetaldehyde	Emissions	68991	80980	149789	84693	628326	318371	298043	379785
	% Emissions	7.4%	8.7%	22.8%	16.2%	63.4%	51.4%	51.1%	54.7%

	Sources Largest	6 32600	9 50282	13 67720	9 72400	14 482560	16 140487	28 138321	34 137019
Acrolein	Emissions	1950	1711	8158	6880	16447	11972	11706	12163
	% Emissions	0.2%	0.2%	1.2%	1.3%	1.7%	1.9%	2.0%	1.8%
	Sources	4	7	13	13	17	20	27	27
	Largest	1910	1539	2282	2565	6698	3196	2676	2720
Formaldehyde	Emissions	859628	850703	498486	431876	346650	288931	273567	302784
	% Emissions	92.4%	91.1%	75.9%	82.5%	35.0%	46.7%	46.9%	43.6%
	Sources	273	294	357	320	301	254	245	266
	Largest	308246	310487	151921	100209	24334	29948	27042	41776
Total Emissions		930569	933394	656433	523448	991423	619274	583317	694732
Total Sources		283	310	383	342	332	290	300	327
Total Largest		308246	310487	151921	100209	482560	140487	138321	137019

Table 28: Reported Emissions from Sources > 1000 Pounds per Year

HAP	Data	1990	1991	1992	1993	1994	1995	1996	1997
Acetaldehyde	Emissions	68753	79947	147011	82704	626809	315519	296991	378477
	% Emissions	7.4%	8.6%	22.4%	15.8%	63.2%	50.9%	50.9%	54.5%
	Sources	3	4	4	2	6	8	14	17
Acrolein	Emissions	1910	1539	7136	6572	15821	9860	8192	9099
	% Emissions	0.2%	0.2%	1.1%	1.3%	1.6%	1.6%	1.4%	1.3%
	Sources	1	1	4	4	6	5	5	5
Formaldehyde	Emissions	833395	814453	446317	380858	298264	241514	225380	254237
	% Emissions	89.6%	87.3%	68.0%	72.8%	30.1%	39.0%	38.6%	36.6%
	Sources	49	59	68	62	61	48	49	51
Total Emissions		904058	895939	600463	470134	940894	566892	530562	641813
Total % Emissions		97.2%	96.0%	91.5%	89.8%	94.9%	91.5%	91.0%	92.4%
Total Sources		53	64	76	68	73	61	68	73

Table 29: Reported Emissions from Sources > 10000 Pounds per Year

HAP	Data	1990	1991	1992	1993	1994	1995	1996	1997
Acetaldehyde	Emissions	68753	62692	137283	82704	619246	308068	264356	359372
	% Emissions	7.4%	6.7%	20.9%	15.8%	62.5%	49.7%	45.3%	51.7%
	Sources	3	2	3	2	4	6	8	11
Formaldehyde	Emissions	719062	662421	262289	231456	124278	129412	94003	133974
	% Emissions	77.3%	71.0%	40.0%	44.2%	12.5%	20.9%	16.1%	19.3%
	Sources	12	14	10	11	7	7	5	7
Total Emissions		787815	725113	399572	314160	743524	437480	358360	493345
Total % Emissions		84.7%	77.7%	60.9%	60.0%	75.0%	70.6%	61.4%	71.0%
Total Sources		15	16	13	13	11	13	13	18

Table 30: Major County Carbonyl Compound Emissions

COUNTY	1990	1991	1992	1993	1994	1995	1996	1997
BROWN Emissions	22452	17402	22695	33888	24698	25899	34412	40849
BROWN % Emissions	2.4%	1.9%	3.5%	6.5%	2.5%	4.2%	5.9%	5.9%
BROWN Sources	9	9	18	14	15	16	15	21

DOUGLAS Emissions	193218	159756	170440	16922	25496	4744	4416	3839
DOUGLAS % Emissions	20.8%	17.1%	26.0%	3.2%	2.6%	0.8%	0.8%	0.6%
DOUGLAS Sources	6	4	6	5	5	3	3	3
LINCOLN Emissions	9451	59890	60164	12344	499198	1892	1617	1527
LINCOLN % Emissions	1.0%	6.4%	9.2%	2.4%	50.4%	0.3%	0.3%	0.2%
LINCOLN Sources	4	7	9	6	6	3	2	2
MARATHON Emissions	29029	64016	36850	8090	6744	151239	168461	147485
MARATHON % Emissions	3.1%	6.9%	5.6%	1.5%	0.7%	24.4%	28.9%	21.2%
MARATHON Sources	11	12	14	11	8	7	9	9
MILWAUKEE Emissions	16628	14187	84337	87261	95022	61818	46198	66517
MILWAUKEE % Emissions	1.8%	1.5%	12.8%	16.7%	9.6%	10.0%	7.9%	9.6%
MILWAUKEE Sources	26	24	34	23	23	27	29	28
OUTAGAMIE Emissions	35583	13651	6790	6989	31749	31633	31518	47194
OUTAGAMIE % Emissions	3.8%	1.5%	1.0%	1.3%	3.2%	5.1%	5.4%	6.8%
OUTAGAMIE Sources	7	6	11	12	12	12	15	15
PRICE Emissions	12270	11934	10624	12630	12301	30237	29266	24309
PRICE % Emissions	1.3%	1.3%	1.6%	2.4%	1.2%	4.9%	5.0%	3.5%
PRICE Sources	3	2	2	2	2	2	3	4
SAWYER Emissions	309446	312695	2635	100745	20356	20444	19891	42134
SAWYER % Emissions	33.3%	33.5%	0.4%	19.2%	2.1%	3.3%	3.4%	6.1%
SAWYER Sources	2	3	3	3	3	2	2	2
WOOD Emissions	34397	41553	7122	11430	101889	149446	98274	125869
WOOD % Emissions	3.7%	4.5%	1.1%	2.2%	10.3%	24.1%	16.8%	18.1%
WOOD Sources	13	8	7	10	12	14	15	16
TOTAL Emissions	662474	695085	401657	290298	817454	477352	434053	499725
TOTAL % Emissions	71.2%	74.5%	61.2%	55.5%	82.5%	77.1%	74.4%	71.9%
TOTAL Sources	81	75	104	86	86	86	93	100

Current WUATM Formaldehyde Data Completeness

Sampling protocols involve collecting one sample every thirty days at the Wisconsin Rapids site, and one sample every six days at the Milwaukee site. The reason for the differential is the clearer legislated level of carbonyl sampling within the PAMS monitoring program, and the different levels of funding available for the programs. Should more funding become available for the WUATM program, sampling frequency should be returned to one in twelve days, which was the standard throughout most of the Green Bay sampling period.

Project completeness with reference to formaldehyde is documented in table 31 below. Completeness is the ratio of valid ambient samples that were submitted to the laboratory, to total Sampling days. Overall project completeness stands at 98.6%, with 73 ambient samples submitted out of a total of 74 possible site sampling days. Missing samples may be due to lack of sampling materials, sampler problems or operator error.

Table 31: Carbonyl Sampling Completeness

Site	Completeness	Samples	Ambient	Void	Blanks	Duplicates	Sampling Days
Witter Field	92.3%	19	12	3	2	2	13
UWM North	100.0%	74	61	1	4	8	61
Overall	98.6%	93	73	4	6	10	74

Analytical completeness is the ratio of results returned to samples submitted. This is documented in the following table. It should be noted that Witter Field results do not always include all parameters, so that the completeness is based on formaldehyde results. Missing samples may be related to laboratory miscommunications, sampler mishandling or operator error.

Table 32: Carbonyl Analytical Completeness

Site	Completeness	Results Returned	Samples Submitted
Witter Field	87.5%	14	16
UWM North	100.0%	73	73
Overall	97.8%	87	89

Analytical Results

Results of current carbonyl analysis are presented in the following tables. It should be noted that this is the last sampling season wherein acetaldehyde and acetone results have been actively requested by the WUATM program. The reasons behind this are related to inconsistently variable results for acetone, which appear to be a function of frequent lab or sampling contamination, and the relatively low toxicity of acetaldehyde. Although we request that random other parameters observed (such as propionaldehyde or acrolein) be reported when they appear to be significant, there were no other parameters reported by the lab this year.

Values reported are in $\mu\text{g}/\text{m}^3$. Averages, maxima, minima and %relative standard deviations are shown, along with the number of samples, the number of detects and the resulting % detection. Non-detects are valued at the detection limit in this section. This is the general convention used in the WUATM to generate maximum potential concentrations for the evaluation of health risks.

Table 33: Wisconsin Rapids Carbonyl Sampling Results

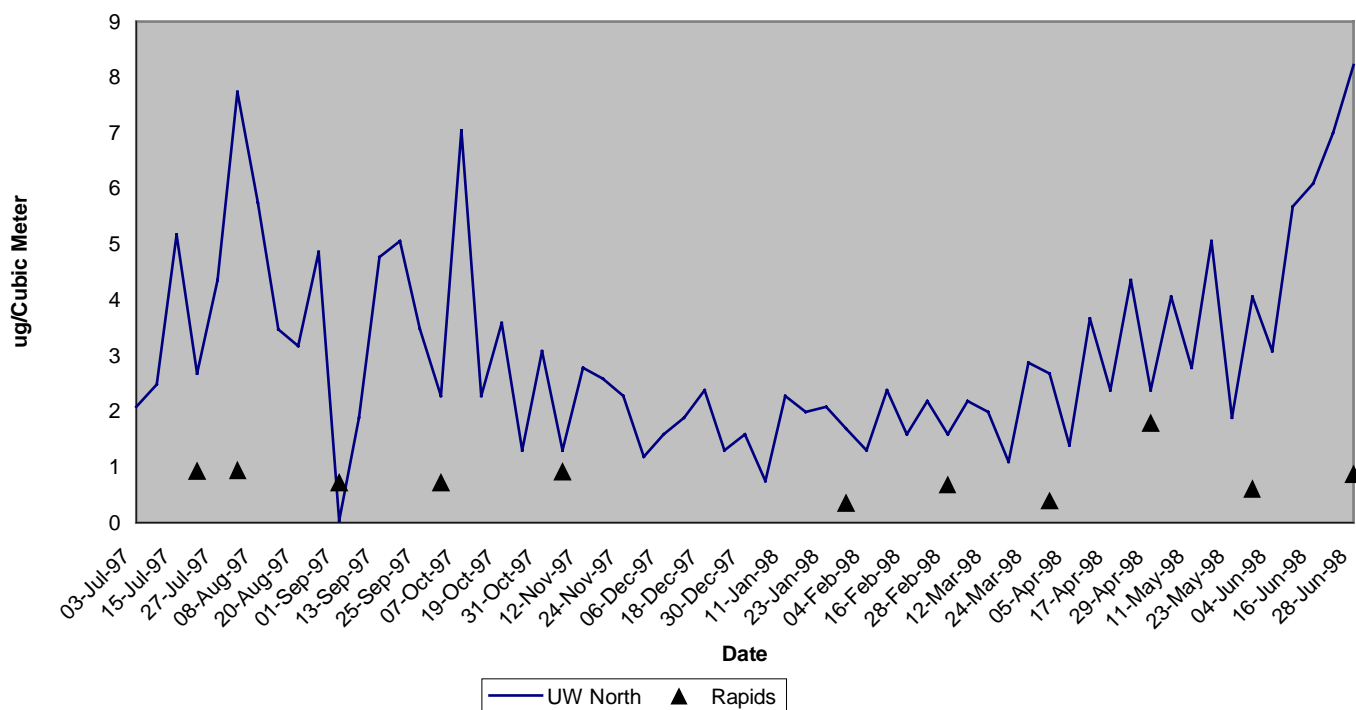
Parameter Name	Average	Maximum	Minimum	%RSD	Detects	Samples	Detection Rate
ACETALDEHYDE	0.63	1.19	0.37	42.1%	7	7	100.0%
ACETONE	1.90	3.49	0.44	55.6%	7	7	100.0%
FORMALDEHYDE	0.77	1.78	0.35	46.5%	13	13	100.0%

Table 34: UW North Carbonyl Sampling Results

Parameter Name	Average	Maximum	Minimum	%RSD	Detects	Samples	Detection Rate
ACETALDEHYDE	1.84	4.77	0.07	53.9%	68	69	98.6%
ACETONE	3.32	7.03	0.88	36.8%	69	69	100.0%
FORMALDEHYDE	3.07	8.22	0.03	58.6%	68	69	98.6%

Concentrations of all carbonyl parameters tend to be higher in Milwaukee than Wisconsin Rapids. This is not surprising considering the higher concentration of mobile and other sources in the Milwaukee urban area.

Figure 11: Milwaukee and Wisconsin Rapids Formaldehyde



The Wisconsin Rapids formaldehyde results are generally compatible with the range of results reported in Green Bay between 1991 and 1997. The Green Bay dataset, however, contains a number of extreme values far higher than any observed to date at Witter Field. This may be related to the lower sampling frequency, and the correspondingly decreased chance of capturing extreme events, or to the location of the former Green Bay site in a public parking lot.

Milwaukee formaldehyde results average slightly higher this year than most previous years. The exception to this is a period between June and August 1994, where all values returned are significantly higher than 15 ug/m^3 , and may well represent sample contamination or temporary local source effects. This year's maximum value exceeds all other values outside of the suspect period.

Quality Assurance Parameters

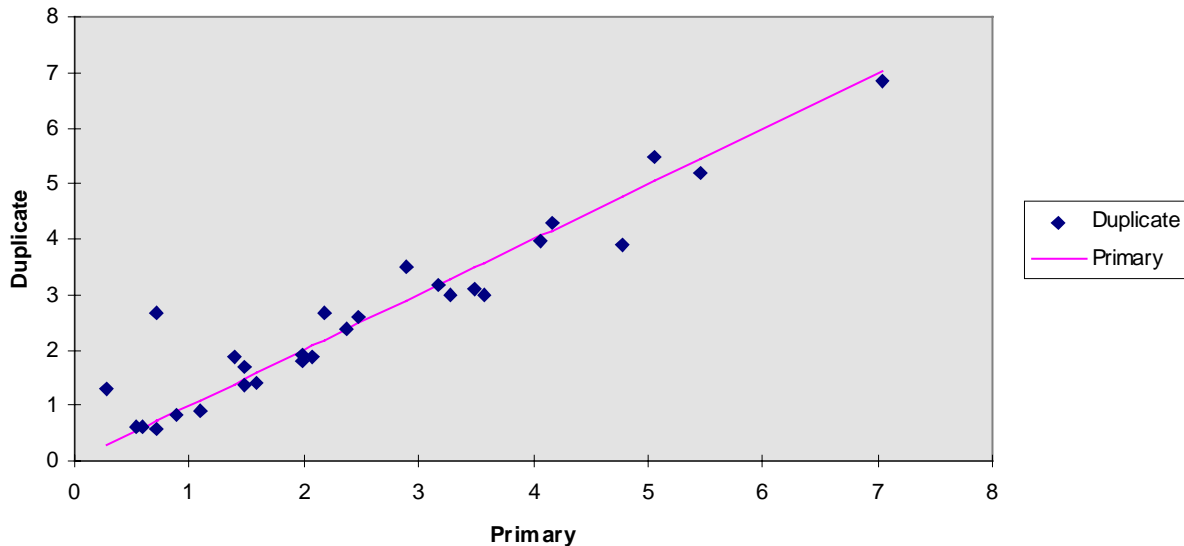
Quality assurance samples obtained include 10 sets of duplicate samples, of which 2 are from Wisconsin Rapids and 8 from Milwaukee. Duplicate analysis includes a total of 28 data pairs, of which all are detect pairs. These results are included in the table for comparison below. A total of 3 pairs (10.7%) exceed $\pm 25\%$. Of these 3 data pairs, one is associated with each parameter.

The acetaldehyde and formaldehyde values in excess of $\pm 25\%$ are from a single Milwaukee sample set, while the acetone data pair is from Wisconsin Rapids. When these values are excluded, the overall average is $\pm 9.9\%$, which is well within the QC goals of $\pm 15\%$. Formaldehyde duplicate precision averages 10.1%.

Table 35: Duplicate Carbonyl Sample Values

Parameter Name	Average	Max	Data Pairs	Over 25%	Average w/o Max
ACETALDEHYDE	21.4%	127.1%	9	1	8.2%
ACETONE	13.4%	30.3%	9	1	11.2%
FORMALDEHYDE	22.8%	115.0%	10	1	10.1%
OVERALL	18.5%	127.1%	28	3	9.9%

Figure 12: Comparison of Primary and Duplicate Analyses



A total of 6 blank samples were submitted this year, with results returned for 1 blank from the WUATM program, and 4 blanks from the 24 hour PAMS sampling regime. Results from these samples are shown in the following table. There were no observed formaldehyde or acetaldehyde concentrations above reporting limits associated with the sampling materials used, while all but one sample which reported acetone (the Rapids analysis did not return this value) was above detection limits. Values observed are of the same magnitude as most ambient results, which tends to invalidate the acetone portion of these results.

Table 36: Blank Carbonyl Sample Results

Sample Date	Formaldehyde	Acetaldehyde	Acetone
30-Jul-97	<0.02	<0.07	0.29
23-Aug-97	<0.02	<0.07	1.3
27-Jan-98	<0.03	<0.07	2.3
20-May-98	<0.02	<0.07	<=0.19
03-Feb-98	<0.02		

Carbonyl Compound Conclusions

Qualitative review of the 24-hour Wisconsin Rapids and Milwaukee formaldehyde sampling and analysis programs yields the following pertinent points of interest:

1. Milwaukee values tend to be higher than values observed in Wisconsin Rapids. Average observed values are about 3.1 and 0.8 $\mu\text{g}/\text{m}^3$, respectively.
2. All Wisconsin Rapids values are less than 2.0 $\mu\text{g}/\text{m}^3$, while most (91.3%) Milwaukee values are less than 6.0 $\mu\text{g}/\text{m}^3$.
3. Wisconsin Rapids results are generally comparable with historic Green Bay values. Milwaukee values are slightly higher this year than previous years, with the maximum higher than almost all previous results. The only results exceeding this value were obtained during a period of questionable quality in 1994.
4. Increasing sample frequency associated with the WUATM program would improve data collection and comparability to the results obtained through the PAMS program.
5. Acetaldehyde and acetone values, although consistently reported as PAMS parameters, have been discontinued as regular WUATM parameters to conserve funds. High blank values obtained for acetone make results for this parameter generally questionable, but acetaldehyde quality control parameters indicate these values are reliable. Returning this parameter to the WUATM parameter list should be considered.

Volatile Organic Compounds

Overview

This broad designation includes a wide variety of compounds, including those in use as solvents, degreasers, gasoline components and products of incomplete combustion. The parameters incorporated into this study are part of a standard suite developed for EPA method TO-14. Most of them are chlorinated solvents, or products of incomplete combustion. Although this parameter list incorporates but a small fraction of potential VOC air contaminants, it includes many of the more potentially hazardous anthropogenic compounds of this class.

VOC testing has been a part of the WUATM program since it's inception in 1991. The original method employed adsorbent tube sampling, followed by thermal desorption and gas chromatographic analysis. This method yielded results of questionable validity, and was superseded by whole air sampling in passivated stainless steel canisters in 1994. Sampling for the toxic VOC parameters in Milwaukee began in January 1997. In addition to the current data, an analysis of Wisconsin Rapids results between 1994 and 1997 is included in this report for project closure.

Volatile Organic Compounds, Data Completeness

Project completeness with reference to VOCs is documented in the following table. Completeness is the ratio of ambient samples collected to total sampling days. It should be noted that the Wisconsin Rapids sampler had a high number of voids associated with site startup and software changes affecting performance. A periodic glitch with the control program causes the sampler to record the stop time before sampling begins, resulting in a void sample. The extra duplicate samples come from repeated attempts to obtain valid samples.

Table 37: VOC Completeness, Wisconsin Rapids

Site	Completeness	Samples	Ambient	Voids	Duplicates	Sample Days
UWMN	100.0%	31	30	0	1	30
Rapids	83.3%	44	25	16	6	30

Volatile Organic Compounds, Toxics Analytical Results

The tables following present a summation of Toxics VOC data. The first table lists all undetected parameters in Wisconsin Rapids and Milwaukee during the course of sampling in 1997 and 1998. A total of 19 parameters were not detected in Wisconsin Rapids, while 22 parameters were not detected in Milwaukee. Parameters detected in Wisconsin Rapids (number of detects in parenthesis) but not in Milwaukee include chlorobenzene (1); chloroform (5); and tetrachloroethene (1). There were no parameters detected in

Milwaukee but not in Wisconsin Rapids.

Table 38: Undetected Parameters in 1997/1998

Parameter Name	Rapids	Milwaukee	Parameter Name	Rapids	Milwaukee
1,1,2,2-TETRACHLOROETHANE	N	N	CHLOROETHANE	N	N
1,1,2-TRICHLOROETHANE	N	N	CHLOROPRENE	N	N
1,2-DICHLOROBENZENE	N	N	CUMENE (i-PROPYLBENZENE)	N	N
1,2-DICHLOROETHANE	N	N	DIBROMOCHLOROMETHANE	N	N
1,2-DICHLOROPROPANE	N	N	METHYLCHLORIDE	N	N
1,3-DICHLOROBENZENE	N	N	STYRENE	N	N
1,4-DICHLOROBENZENE	N	N	TRICHLOROETHENE	N	N
BROMODICHLOROMETHANE	N	N	VINYLCHLORIDE	N	N
BROMOFORM	N	N	CHLOROBENZENE	Y	N
BROMOMETHANE	N	N	CHLOROFORM	Y	N
c-1,3-DICHLOROPROPENE	N	N	TETRACHLOROETHENE	Y	N

The following two tables present results from those samples which were detected at least once during the year in Wisconsin Rapids and Milwaukee, respectively. Evaluation criteria are average, maximum, and minimum reported values, along with percent relative standard deviation. Additional reporting criteria include the number of detects, and how many samples reported each particular parameter. Values are reported as ppbv.

Table 39: Wisconsin Rapids Toxics VOC Results (ppbv)

Parameter	Average	Maximum	Minimum	%RSD	Detects	Samples	Detection Rate
ACETYLENE	1.03	3.30	0.33	63.8%	30	30	100.0%
BENZENE	0.28	0.70	0.09	53.7%	30	30	100.0%
TOLUENE	0.50	1.10	0.15	54.0%	30	30	100.0%
PROPENE	0.28	0.87	0.12	59.7%	27	30	90.0%
XYLENES (m & p)	0.23	0.50	0.10	55.7%	24	30	80.0%
ETHYLBENZENE	0.09	0.15	0.05	34.7%	16	30	53.3%
o-XYLENE	0.11	0.17	0.05	36.5%	14	30	46.7%
CARBON TETRACHLORIDE	0.10	0.12	0.10	7.5%	7	30	23.3%
CHLOROFORM	0.24	0.37	0.14	35.7%	5	30	16.7%
METHYLENE CHLORIDE	0.20	0.43	0.11	80.4%	4	30	13.3%
1,1,1-TRICHLOROETHANE	0.10	0.10	0.10	0.0%	2	30	6.7%
1,3 BUTADIENE		0.15			1	30	3.3%
CHLOROBENZENE		0.10			1	30	3.3%
n-OCTANE		0.14			1	30	3.3%
TETRACHLOROETHENE		0.15			1	30	3.3%

Table 40: Milwaukee Toxics VOC Results (ppbv)

Parameter	Average	Maximum	Minimum	%RSD	Detects	Samples	Detection Rate
ACETYLENE	1.89	7.90	0.30	79.8%	31	31	100.0%
BENZENE	0.38	0.95	0.14	50.3%	30	31	96.8%
PROPENE	0.44	0.98	0.12	54.4%	30	31	96.8%
TOLUENE	0.84	2.80	0.16	69.9%	30	31	96.8%

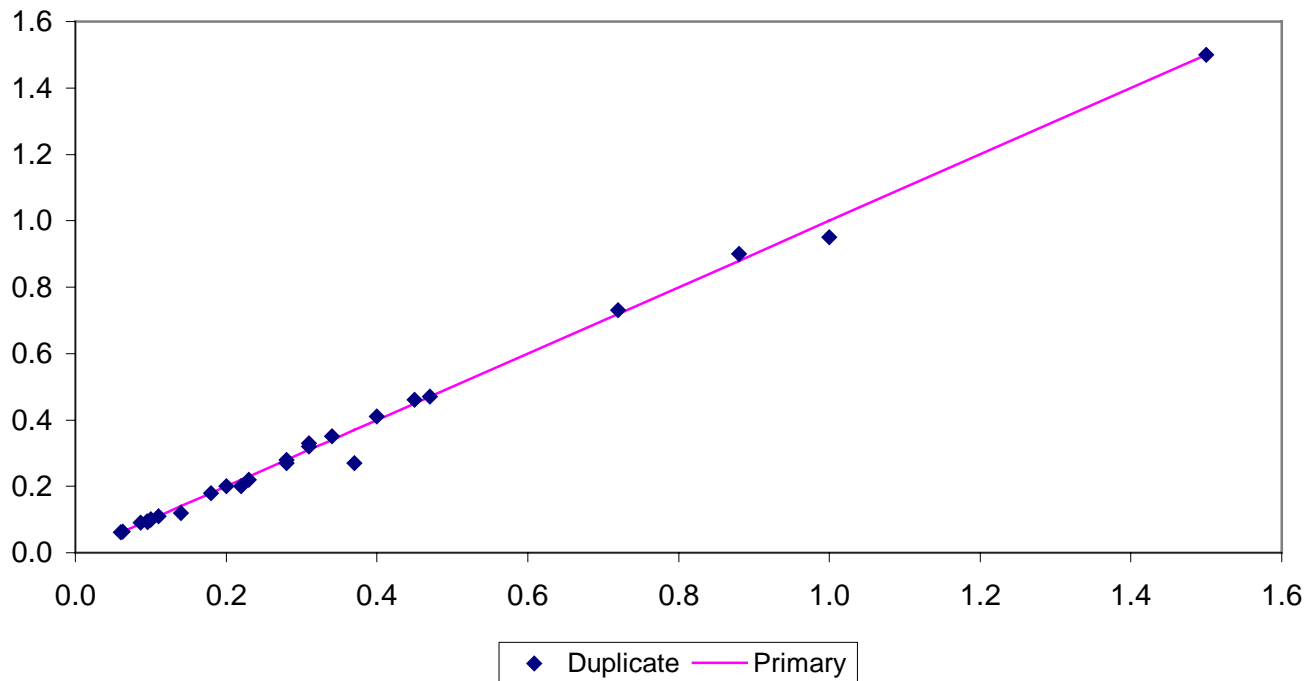
ETHYLBENZENE	0.12	0.29	0.05	45.2%	25	31	80.6%
XYLENES (m & p)	0.39	1.10	0.11	55.3%	25	31	80.6%
o-XYLENE	0.14	0.40	0.05	55.9%	24	31	77.4%
METHYLENE CHLORIDE	0.20	0.38	0.10	39.5%	20	31	64.5%
CARBON TETRACHLORIDE	0.11	0.11	0.10	5.2%	6	31	19.4%
1,3 BUTADIENE	0.13	0.17	0.11	19.5%	5	31	16.1%
1,1,1-TRICHLOROETHANE	0.12	0.14	0.11	14.4%	3	31	9.7%
n-OCTANE	0.06	0.08	0.06	20.6%	3	31	9.7%

Volatile Organic Compounds, Quality Assurance Parameters

The primary quality control samples collected during 1997 and 1998 were duplicate samples. Wisconsin Rapids and Milwaukee samples in this category are considered together. A total of 3 duplicate sample sets were collected in Wisconsin Rapids, while 1 was collected in Milwaukee. The graph below shows a comparison of duplicate samples analyzed for toxics parameters.

A total of 136 data pairs are represented in this table, of which 26 are detect pairs (19.1%). There were no unacceptable pairs. Non-detect pairs show qualitative agreement and are not incorporated into the graph. The average percent difference between the detect pairs is 3.9%. There is 1 detect pair (0.7%) which fails the quality control limit of $\pm 25\%$. The magnitude of this pair's difference is 0.1 ppbv. Overall, the duplicates indicate that the samplers are functioning well within quality control parameters.

Figure 13: VOC Duplicate Detect Pairs



A total of 136 data pairs are represented in this table, of which 26 are detect pairs (19.1%). There were no unacceptable pairs. Non-detect pairs show qualitative agreement and are not incorporated into the graph. The average percent difference between the detect pairs is 3.9%. There is 1 detect pair (0.7%) which fail the quality control limit of $\pm 25\%$. The magnitude of this pair's difference is 0.1 ppbv.

Table 41: VOC Duplicate Values

Site	Parameter	Primary	Duplicate	Average	% Diff
Witter	CHLOROFORM	0.4	0.3	0.3	31.3%
UWM	PROPENE	0.1	0.1	0.1	15.4%
UWM	BENZENE	0.2	0.2	0.2	9.5%
Witter	PROPENE	0.3	0.3	0.3	6.3%
UWM	ACETYLENE	1.0	1.0	1.0	5.1%
Witter	ETHYLBENZENE	0.1	0.1	0.1	4.5%
UWM	METHYLENE CHLORIDE	0.2	0.2	0.2	4.4%
Witter	PROPENE	0.3	0.3	0.3	3.6%
Witter	o-XYLENE	0.1	0.1	0.1	3.3%
Witter	BENZENE	0.1	0.1	0.1	3.2%
Witter	BENZENE	0.3	0.3	0.3	3.2%
Witter	BENZENE	0.3	0.4	0.3	2.9%
Witter	ACETYLENE	0.4	0.4	0.4	2.5%
Witter	ACETYLENE	0.9	0.9	0.9	2.2%
Witter	TOLUENE	0.5	0.5	0.5	2.2%
Witter	TOLUENE	0.7	0.7	0.7	1.4%
Witter	ETHYLBENZENE	0.1	0.1	0.1	0.0%
Witter	o-XYLENE	0.1	0.1	0.1	0.0%

Witter	1,1,1-TRICHLOROETHANE	0.1	0.1	0.1	0.0%
Witter	CARBON TETRACHLORIDE	0.1	0.1	0.1	0.0%
Witter	XYLENES (m & p)	0.1	0.1	0.1	0.0%
Witter	XYLENES (m & p)	0.2	0.2	0.2	0.0%
UWM	TOLUENE	0.2	0.2	0.2	0.0%
Witter	XYLENES (m & p)	0.3	0.3	0.3	0.0%
Witter	TOLUENE	0.5	0.5	0.5	0.0%
Witter	ACETYLENE	1.5	1.5	1.5	0.0%

Analysis of field blanks has not been incorporated directly into the WUATM VOC sampling scheme. Part of the analysis contract specifies that canisters be cleaned to <10 ppbc total, with individual target compounds present only at less than 0.1 ppb.

VOC Data Comparisons

An inter-site comparison has been conducted for the 6 most detected parameters (acetylene, benzene, ethylbenzene, propene, toluene and xylenes (m&p)). The following graph displays the average values for each of these parameters. Statistical analysis of site differences was conducted by using standard t-tests. All parameters show significant differences between the sites. Table 42 on the following page summarizes the statistical parameters from the inter-site comparison.

Figure 14: Most Detected VOC Parameters

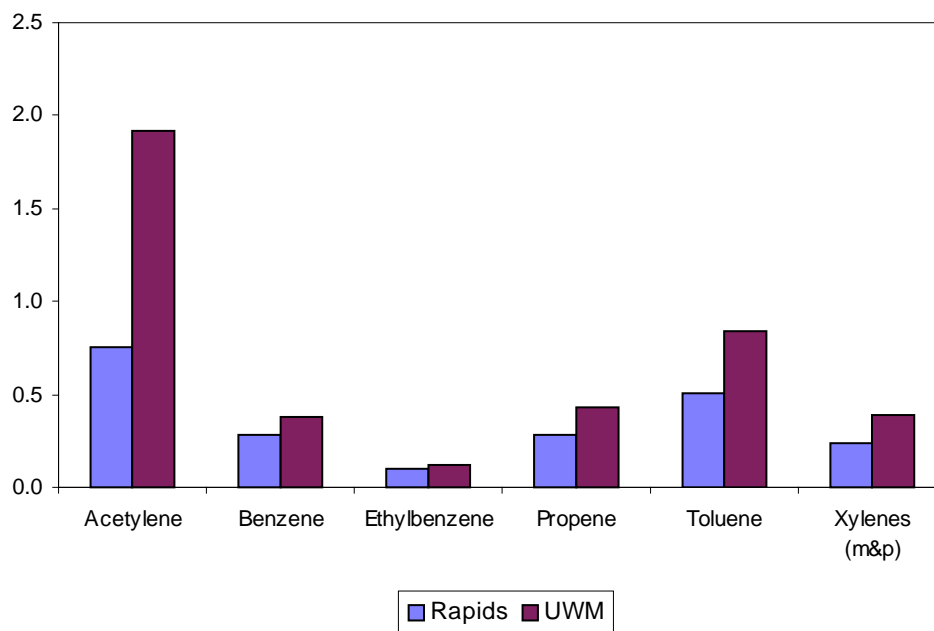


Table 42: t-Test Results, Most Detected Parameters

Parameter	Samples	t =	probability
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Acetylene	30	3.411	0.002
Benzene	30	2.529	0.017
Ethyl Benzene	16	2.307	0.036
Propene	27	3.691	0.001
Toluene	30	2.999	0.006
Xylenes (m&p)	24	3.147	0.005

The table below summarizes the data from the remaining detected parameters. Statistical analysis of these results was not performed because of the few samples which returned detects on the same sampling day.

Table 43: Low Detection Rate Parameter Comparison

Parameter	Rapids Average	Rapids Maximum	UWM Average	UWM Maximum
o-XYLENE	0.11	0.17	0.14	0.40
CARBON TETRACHLORIDE	0.10	0.12	0.11	0.11
CHLOROFORM	0.24	0.37		
METHYLENE CHLORIDE	0.20	0.43	0.20	0.38
1,1,1-TRICHLOROETHANE	0.10	0.10	0.12	0.14
1,3 BUTADIENE		0.15	0.13	0.17
CHLOROBENZENE		0.10		
n-OCTANE		0.14	0.06	0.08
TETRACHLOROETHENE		0.15		

Volatile Organic Compound Conclusions

Analysis of the volatile organic compound results yields the following pertinent points of interest:

1. Fifteen of the thirty four parameters were detected at least once in Wisconsin Rapids during the 1997/1998 project year. Twelve of the parameters were detected at least once in Milwaukee.
2. The six most frequently detected parameters were the same between the two sites. All of these compounds are products of incomplete combustion; no chlorinated compounds are among them.
3. Statistical analysis of the sets of most frequently detected compound results reveals that the concentrations of these parameters are higher in Milwaukee than in Wisconsin Rapids. This conclusion is consistent with higher vehicle emissions in the Milwaukee area.
4. Insufficient data is present for yearly or seasonal trends at this point.

Sulfur Gases

Overview

Gaseous sulfur compounds can include both oxidized sulfur (SO_2 and sulfuric acid) and reduced sulfur gases such as hydrogen sulfide or methyl mercaptan. SO_2 is a criteria pollutant with an EPA established ambient air quality limit of 0.140 ppm over a 24-hour period. This parameter is not normally included with toxics monitoring because of its criteria pollutant status.

The reduced compounds are strongly odoriferous and can be frequently be smelled at concentrations in the low ppb. In addition to their nuisance value they have associated toxic effects, although the concentrations that these occur tend to be significantly higher than their odor thresholds.

These compounds are frequently associated with paper mills and sewage treatment plants, providing their characteristic odor. The numerous paper mills in the Wisconsin Rapids area led to the inclusion of this class of compounds into the parameter list. There are numerous methods for their determination in the ambient air.

The approach adopted by WUATM has been to determine total sulfur on a continuous basis, using an oxidation catalyst to convert the reduced sulfur compounds to SO_2 , followed by a Monitor Labs 8850 SO_2 analyzer. A second SO_2 analyzer without a catalyst is operated side by side with the total sulfur analyzer, to determine the SO_2 content. The reduced sulfur content can then be determined by subtraction.

Variation between the instruments may lead to a situation of “greater” SO_2 than Total Sulfur, leading to a “negative” TRS value. Though the general detection limit for these monitors is 0.002 ppm, the combination of monitors affects the ability to detect low levels of TRS. Reliable detection limits using this method are regarded as 0.005 ppm TRS, which is above the odor threshold.

It is important to note that the data in this section covers the period beginning at the start of monitoring, through the end of 1998. This departure from the general reporting mode of the WUATM program is made because the continuous data collection leads to more up to date data reduction than laboratory analysis allows for. Reliable data collection for these parameters began in December 1997.

Parameter Sources

Sulfur dioxide is a naturally occurring oxide of sulfur that can be emitted from both anthropogenic and natural sources. It is estimated that less than 30% of global emissions are from anthropogenic sources. Most anthropogenic SO_2 released to the atmosphere is associated with the combustion of fossil fuels in power generation and industrial activities. Another potential source is the oxidation of reduced sulfur compounds.

Sulfur dioxide is readily oxidized to sulfur trioxide and sulfate in the air through

interactions with a variety of other gases, or by direct photochemical reactions. The estimated atmospheric residence time is about 10 days. SO₂ is also highly soluble in water, where it contributes to acid rain formation. The fate of these compounds is typically removal through wet or dry deposition, or absorption by plants.

Hydrogen sulfide (H₂S) is the primary reduced sulfur compound typically encountered. It has a characteristic “rotten egg” odor that is detectable at low part per billion levels in the atmosphere. It is a naturally occurring gas that is produced through anaerobic reduction of sulfates and sulfur containing organic compounds. It is estimated that 90% of the total H₂S in the atmosphere is emitted from natural sources, such as swamps and bogs.

Anthropogenic production of H₂S includes synthesis for use in rayon manufacture and as an additive in lubricants and cutting oils. It is a byproduct of kraft pulp and paper manufacturing, and may be produced in landfills and manure pits through anaerobic digestion processes. This compound is typically oxidized to SO₂, and has an atmospheric lifetime ranging from less than a day to as high as 42 days in winter.

Carbon disulfide (CS₂) is another common reduced sulfur compound. In its pure state, it is a highly volatile liquid with a strong odor. It is produced naturally in small quantities by microbial action in soils and wetlands, but the majority of emissions are thought to be anthropogenic. This compound is used in the production of rayon and carbon tetrachloride, along with a variety of smaller uses. Releases to the atmosphere are associated with these industrial processes, and combustion of fossil fuels.

Methyl mercaptan is another common reduced sulfur compound. It is a naturally occurring compound produced through bacterial degradation of organic material, and is also present in natural gas. Anthropogenic sources include wood pulp, oil shale and petroleum refining processes and sewage treatment plants. This compound, along with H₂S and several other chemicals, is part of the Total Reduced Sulfur determinations made at pulp and refining operations.

Reported Emissions

Industrial sources which emit quantities of toxic materials above particular limits are required to report their emissions to the DNR. Reporting requirements have varied, and all potential sources may not be identified. The reported emissions are typically estimated based on process material throughput and standard emission factors which have been developed by the EPA. Significant variation among facilities operating similar equipment is common, and may not be reflected in the standard emission factors.

These factors render reported emissions data useful mostly as an order of magnitude estimate of industrial emissions. Reported toxic releases both statewide, and in selected counties, between 1993 and 1997 are summarized in the table below. Emissions for most compounds are in pounds per year. Sulfur dioxide emissions are in tons per year.

Table 44: Statewide Sulfur Dioxide Emissions

Sulfur Dioxide	Year				
Data	1993	1994	1995	1996	1997
Emissions	248492.2	264695.7	250612.5	257615.4	295426.2
Sources	900	931	1367	1466	1522
>1000 Tons					
Emissions	233889.7	251346.9	237756.7	245176.5	283909.0
Percent of Total	94.1%	95.0%	94.9%	95.2%	96.1%
Sources	28	28	27	27	28
Percent of Sources	3.1%	3.0%	2.0%	1.8%	1.8%
>10000 Tons					
Emissions	156703.6	171587.2	167352.3	168385.4	210690.1
Percent of Total	63.1%	64.8%	66.8%	65.4%	71.3%
Sources	8	9	9	8	9
Percent of Sources	0.9%	1.0%	0.7%	0.5%	0.6%

Table 45: Top Ten Sulfur Dioxide Emitting Counties

County	Data	1993	1994	1995	1996	1997
BROWN	Emissions	26438.8	25392.9	24369.5	24889.1	25882.4
	Percent of Total	10.6%	9.6%	9.7%	9.7%	8.8%
	Sources	35	42	44	46	50
COLUMBIA	Emissions	28246.2	25440.3	31352.7	33277.2	51692.7
	Percent of Total	11.4%	9.6%	12.5%	12.9%	17.5%
	Sources	10	12	13	14	13
KENOSHA	Emissions	27107.6	27368.9	27404.0	30689.5	29963.0
	Percent of Total	10.9%	10.3%	10.9%	11.9%	10.1%
	Sources	13	17	17	17	16
MARATHON	Emissions	11947.0	11322.8	12270.7	13447.9	13602.3
	Percent of Total	4.8%	4.3%	4.9%	5.2%	4.6%
	Sources	24	24	32	33	34
MILWAUKEE	Emissions	34851.8	34965.3	40170.9	47245.4	58172.1
	Percent of Total	14.0%	13.2%	16.0%	18.3%	19.7%
	Sources	89	92	99	109	107
OUTAGAMIE	Emissions	10732.1	11990.8	11664.1	11402.2	12536.5
	Percent of Total	4.3%	4.5%	4.7%	4.4%	4.2%
	Sources	22	24	28	32	30
OZAUKEE	Emissions	3371.6	6222.5	11357.0	9620.1	12938.7
	Percent of Total	1.4%	2.4%	4.5%	3.7%	4.4%
	Sources	13	12	12	14	17
SHEBOYGAN	Emissions	30801.0	30710.4	17260.1	19699.6	18538.1
	Percent of Total	12.4%	11.6%	6.9%	7.6%	6.3%
	Sources	18	23	27	30	35
VERNON	Emissions	9549.9	12889.9	13360.6	10420.1	11698.7
	Percent of Total	3.8%	4.9%	5.3%	4.0%	4.0%
	Sources	2	2	2	2	2
WOOD	Emissions	13409.4	15517.5	14675.8	15724.4	15946.3
	Percent of Total	5.4%	5.9%	5.9%	6.1%	5.4%
	Sources	19	19	18	19	18

Table 46: Other Reported Sulfur Gas Emissions

Parameter	Data	1993	1994	1995	1996	1997
Carbon disulfide (CS ₂)	Emissions	257405.6	300443.0	277595.0	300877.2	296878.5
	Percent of Total	8.9%	8.3%	7.9%	8.5%	5.6%
	Sources	2	2	1	4	3
Carbonyl sulfide (COS)	Emissions	9480.0	11555.0	9728.0	11648.2	10980.0
	Percent of Total	0.3%	0.3%	0.3%	0.3%	0.2%
	Sources	1	2	1	3	1
Dimethyl sulfate	Emissions	16.0	10.0	7.9		0.8
	Percent of Total	0.0%	0.0%	0.0%	0.0%	0.0%
	Sources	1	2	2		1
Hydrogen sulfide (H ₂ S)	Emissions	112260.5	274043.8	282255.4	233308.5	371425.9
	Percent of Total	3.9%	7.6%	8.0%	6.6%	7.0%
	Sources	5	6	9	9	12
Sulfuric acid (H ₂ SO ₄)	Emissions	1379745.8	2039420.9	1858204.4	1872807.9	2477720.0
	Percent of Total	47.7%	56.3%	52.6%	52.9%	46.9%
	Sources	48	36	39	38	44
Total Reduced Sulfur (TRS)	Emissions	1134679.8	997787.7	1107013.4	1120456.4	2127775.1
	Percent of Total	39.2%	27.5%	31.3%	31.7%	40.3%
	Sources	4	5	7	6	10
Total Sum of Emissions		2893587.7	3623260.5	3534804.2	3539098.2	5284780.3
Total Count of Source Name		61	53	59	60	71
>10000 Lbs						
Carbon disulfide	Emissions	257400.0	300146.0	277595.0	299912.0	296276.0
	Percent of Total	8.9%	8.3%	7.9%	8.5%	5.6%
	Sources	1	1	1	1	1
Carbonyl sulfide	Emissions		11518.0		11245.0	10980.0
	Percent of Total	0.0%	0.3%	0.0%	0.3%	0.2%
	Sources		1		1	1
Hydrogen sulfide	Emissions	105998.2	266641.8	267029.6	225508.9	342570.5
	Percent of Total	3.7%	7.4%	7.6%	6.4%	6.5%
	Sources	3	4	6	5	6
Sulfuric acid	Emissions	1319752.2	1987548.0	1816814.0	1823238.2	2450585.2
	Percent of Total	45.6%	54.9%	51.4%	51.5%	46.4%
	Sources	12	12	13	12	15
Total Reduced Sulfur	Emissions	1134679.8	997787.7	1106368.6	1120456.4	2127578.2
	Percent of Total	39.2%	27.5%	31.3%	31.7%	40.3%
	Sources	4	5	6	6	9
Total Sum of Emissions		2817830.3	3563641.5	3467807.2	3480360.6	5227989.9
Percent of Total		97.4%	98.4%	98.1%	98.3%	98.9%
Total Count of Sources		20	23	26	25	32
>100,000 lbs						
Carbon disulfide	Emissions	257400.0	300146.0	277595.0	299912.0	296276.0
	Percent of Total	8.9%	8.3%	7.9%	8.5%	5.6%
	Sources	1	1	1	1	1
Hydrogen sulfide	Emissions		104329.0			146531.0
	Percent of Total	0.0%	2.9%	0.0%	0.0%	2.8%
	Sources		1			1
Sulfuric acid	Emissions	1178191.6	1840989.0	1690413.2	1524821.3	2160116.4
	Percent of Total	40.7%	50.8%	47.8%	43.1%	40.9%
	Sources	6	6	6	4	6
Total Reduced Sulfur	Emissions	965000.0	859382.0	1030057.9	970094.4	2000020.7
	Percent of Total	33.3%	23.7%	29.1%	27.4%	37.8%
	Sources	1	3	4	3	5
Total Sum of Emissions		2400591.6	3104846.0	2998066.2	2794827.7	4602944.2
Percent of Total		83.0%	85.7%	84.8%	79.0%	87.1%
Total Count of Sources		8	11	11	8	13

Table 47: Other Sulfur Gas Emissions, Top 8 Counties

County	HAP	Data	1993	1994	1995	1996	1997
BROWN	H2SO4	Emissions	541480.6	562630.4	635904.2	582262.8	577556.8
		Percent	18.7%	15.5%	18.0%	16.5%	10.9%
		Sources	5	6	5	4	4
CRAWFORD	CS2	Emissions	257400.0	300146.0	277595.0	299912.0	296276.0
		Percent	8.9%	8.3%	7.9%	8.5%	5.6%
		Sources	1	1	1	1	1
	COS	Emissions	9480.0	11518.0	9728.0	11245.0	10980.0
		Percent	0.3%	0.3%	0.3%	0.3%	0.2%
		Sources	1	1	1	1	1
CRAWFORD		Emissions	266880.0	311664.0	287323.0	311157.0	313337.0
CRAWFORD		Percent	9.2%	8.6%	8.1%	8.8%	5.9%
CRAWFORD		Sources	2	2	2	2	3
MARATHON	H2S	Emissions	20302.2	19770.3	21208.7	21471.8	25253.4
		Percent	0.7%	0.5%	0.6%	0.6%	0.5%
		Sources	1	1	1	1	1
	H2SO4	Emissions	15031.7	17718.6	13568.3	16153.0	22074.5
		Percent	0.5%	0.5%	0.4%	0.5%	0.4%
		Sources	4	4	5	5	5
TRS	Emissions	39327.8	38855.1	41270.6	40851.4	42041.9	
	Percent	1.4%	1.1%	1.2%	1.2%	0.8%	
	Sources	1	1	1	1	1	
MARATHON		Emissions	74661.8	76344.0	76047.7	78476.2	89369.8
MARATHON		Percent	2.6%	2.1%	2.2%	2.2%	1.7%
MARATHON		Sources	6	6	7	7	7
MARINETTE	H2SO4	Emissions	142787.7	146080.7	124514.0	100679.7	114440.5
		Percent	4.9%	4.0%	3.5%	2.8%	2.2%
		Sources	4	3	3	2	2
ONEIDA	H2SO4	Emissions	112219.6	120736.0	117451.2	88159.0	97667.0
		Percent	3.9%	3.3%	3.3%	2.5%	1.8%
		Sources	1	1	1	1	1
OUTAGAMIE	H2S	Emissions		51165.8	51313.7	48656.8	52167.6
		Percent	0.0%	1.4%	1.5%	1.4%	1.0%
		Sources		1	1	1	1
	H2SO4	Emissions	39791.7	43759.0	43799.1	43433.5	79338.2
		Percent	1.4%	1.2%	1.2%	1.2%	1.5%
		Sources	3	2	3	3	3
TRS	Emissions	72902.0	99550.6	126197.9	95070.8	102010.1	
	Percent	2.5%	2.7%	3.6%	2.7%	1.9%	
	Sources	1	1	1	1	2	
OUTAGAMIE		Emissions	112693.7	194475.4	221310.7	187161.1	233515.8
OUTAGAMIE		Percent	3.9%	5.4%	6.3%	5.3%	4.4%
OUTAGAMIE		Sources	4	4	5	5	6
SHEBOYGAN	H2SO4	Emissions					448305.0
		Percent	0.0%	0.0%	0.0%	0.0%	8.5%
		Sources					1
	TRS	Emissions		235106.0	173400.0	247000.0	208400.0
		Percent	0.0%	6.5%	4.9%	7.0%	3.9%
		Sources		1	1	1	1
SHEBOYGAN		Emissions	5.9	235106.2	173400.1	247000.0	656705.0
SHEBOYGAN		Percent	0.0%	6.5%	4.9%	7.0%	12.4%
SHEBOYGAN		Sources	2	3	2	1	2
WOOD	H2S	Emissions	85696.0	195705.7	159467.1	155380.4	230109.6
		Percent	3.0%	5.4%	4.5%	4.4%	4.4%
		Sources	2	2	3	3	3
	H2SO4	Emissions	467252.0	1090418.0	882440.6	982061.3	1055560.1
		Percent	16.1%	30.1%	25.0%	27.7%	20.0%
		Sources	4	4	4	4	4
TRS	Emissions	1022450.0	624276.0	765500.0	737534.3	802671.2	
	Percent	35.3%	17.2%	21.7%	20.8%	15.2%	
	Sources	2	2	3	3	4	
WOOD		Emissions	1575398.0	1910733.7	1807407.7	1874975.9	2088340.9
WOOD		Percent	54.4%	52.7%	51.1%	53.0%	39.5%
WOOD		Sources	8	10	10	10	11

Sulfur Gas Results Summary

Data is collected on a minute average basis, a major departure from the general SO₂

monitoring protocol, which collects data on an hourly average basis. This provides more comprehensive information, as the majority of events associated with these gases are of short duration. Completeness under these conditions is then based on the ratio of recorded valid ambient minutes to the total number of minutes. The table below documents the completeness on a monthly and overall basis. Additionally, the percentage of all on-line Total Sulfur and Total Reduced Sulfur values greater than 0.002 ppm are included in this table.

Table 48: Sulfur Gas Completeness by Month

Completeness	TS >0.002	TRS >0.002
Jan-98	67.6%	9.9%
Feb-98	93.5%	23.6%
Mar-98	80.1%	21.4%
Apr-98	93.4%	23.2%
May-98	89.6%	29.1%
Jun-98	95.0%	28.9%
Jul-98	94.1%	13.2%
Aug-98	63.1%	7.0%
Sep-98	89.2%	15.0%
Oct-98	94.3%	20.7%
Nov-98	90.3%	21.2%
Dec-98	95.3%	30.8%
Average	87.1%	20.3%

Monthly sulfur data report memos are prepared for this site, compiling all data collected during the month and examining completeness, hourly averages greater than 0.050 ppm, and TRS events greater than 0.005 ppm. Graphs incorporating all minutes where total sulfur exceeds 0.002 ppm are prepared to help visually evaluate the parameter trends. The table below reports all hourly averages greater than 0.100 ppm.

Table 50: Rapids Total Sulfur Hours Over 0.100 ppm

Date and Time	Total Sulfur	Sulfur	Wind
12/15/97 12:00 AM	0.195	0.196	208
10/26/98 10:00 AM	0.192	0.195	221
12/15/97 01:00 AM	0.139	0.141	211
10/24/98 12:00 AM	0.130	0.130	201
05/17/98 08:00 AM	0.123	0.124	206
12/15/97 07:00 AM	0.119	0.121	203
10/23/98 11:00 PM	0.114	0.113	201
12/15/97 06:00 AM	0.107	0.108	207
10/23/98 10:00 PM	0.105	0.104	201

Data to date has shown that the majority of the sulfur gas events are composed primarily of SO₂, although there are some major exceptions to this. The following table documents all hours during 1997 and 1998 where total reduced sulfur (TRS) is greater than 0.010 ppm.

Table 51: Rapids TRS Hours Over 0.010 ppm

Date and Time	Total Sulfur	Sulfur	TRS	Wind
4/18/98 12:00 AM	0.016	0.001	0.015	217
3/30/98 07:00 AM	0.016	0.001	0.015	244
3/30/98 5:00 AM	0.018	0.003	0.015	210
4/18/98 5:00 AM	0.019	0.005	0.014	166
10/23/98 6:00 AM	0.012	0.001	0.011	208
5/26/98 5:00 AM	0.024	0.014	0.010	205

The following table presents all daily sulfur averages greater than or equal to 0.010 ppm.

Table 52: 24-Hour Average Sulfur Concentrations

Date	Total Sulfur	SO2	Date	Total Sulfur	SO2
15-Dec-97	0.048	0.047	17-May-98	0.013	0.012
10-Sep-98	0.034	0.034	01-Jun-98	0.013	0.011
24-Oct-98	0.030	0.030	11-Dec-98	0.013	0.012
23-Oct-98	0.017	0.014	11-Sep-98	0.010	0.010
26-Oct-98	0.016	0.017	13-Jul-98	0.010	0.012
03-Dec-98	0.015	0.015	13-Mar-98	0.010	0.010
23-Dec-98	0.014	0.014	25-Oct-98	0.009	0.010
25-Nov-98	0.013	0.014			

The following graphs illustrate the daily and hourly averages throughout the testing period. Each graph incorporates daily or hourly average data for total sulfur, SO₂, and wind direction. All Total Sulfur values greater than 0.100 ppm are noted. Wind direction values less than 150 degrees have had 360 added to them to prevent significant overlap with sulfur gas traces.

Figure 15: Daily Sulfur Values 12/97 through 12/98

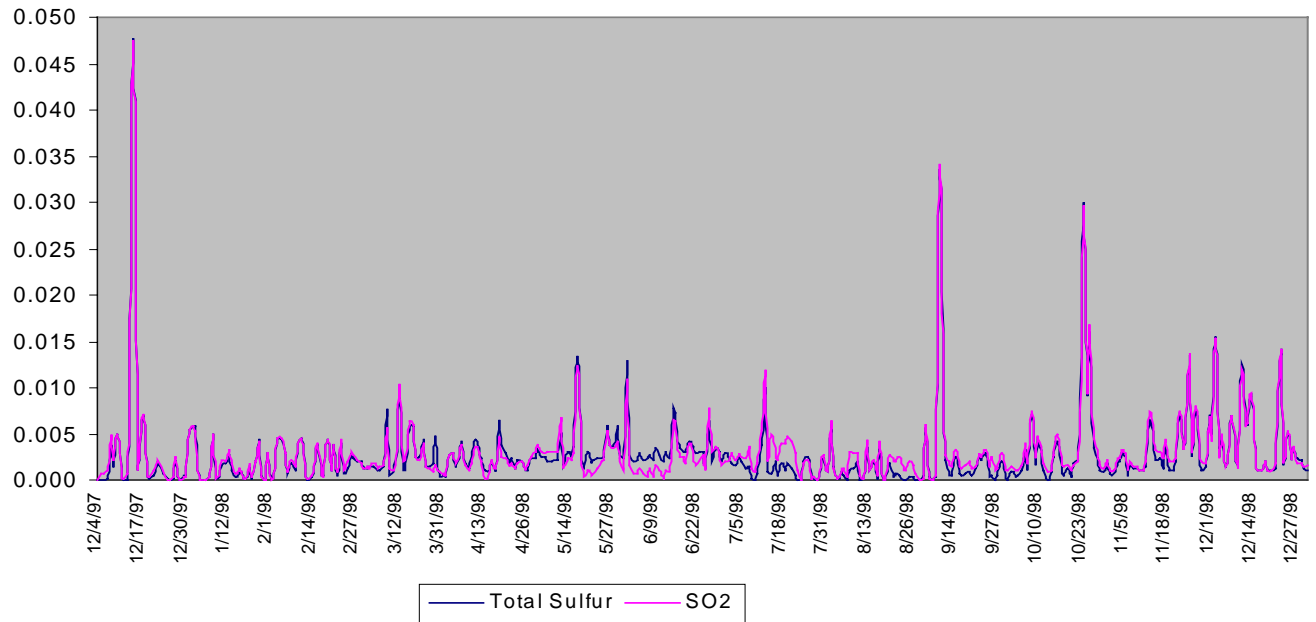
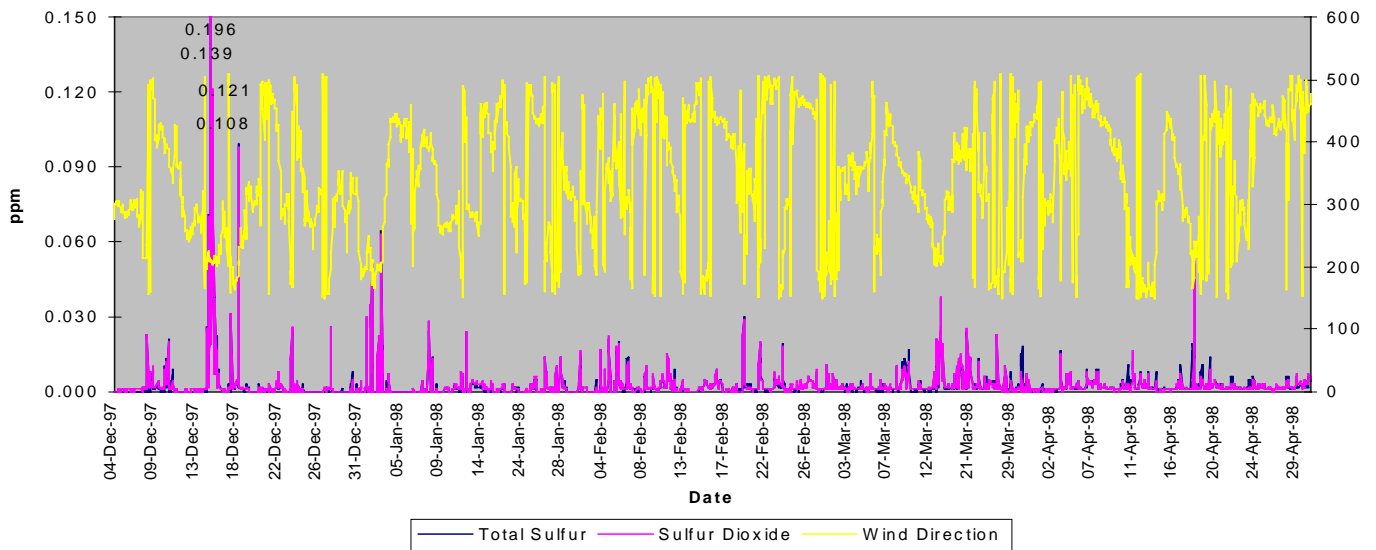
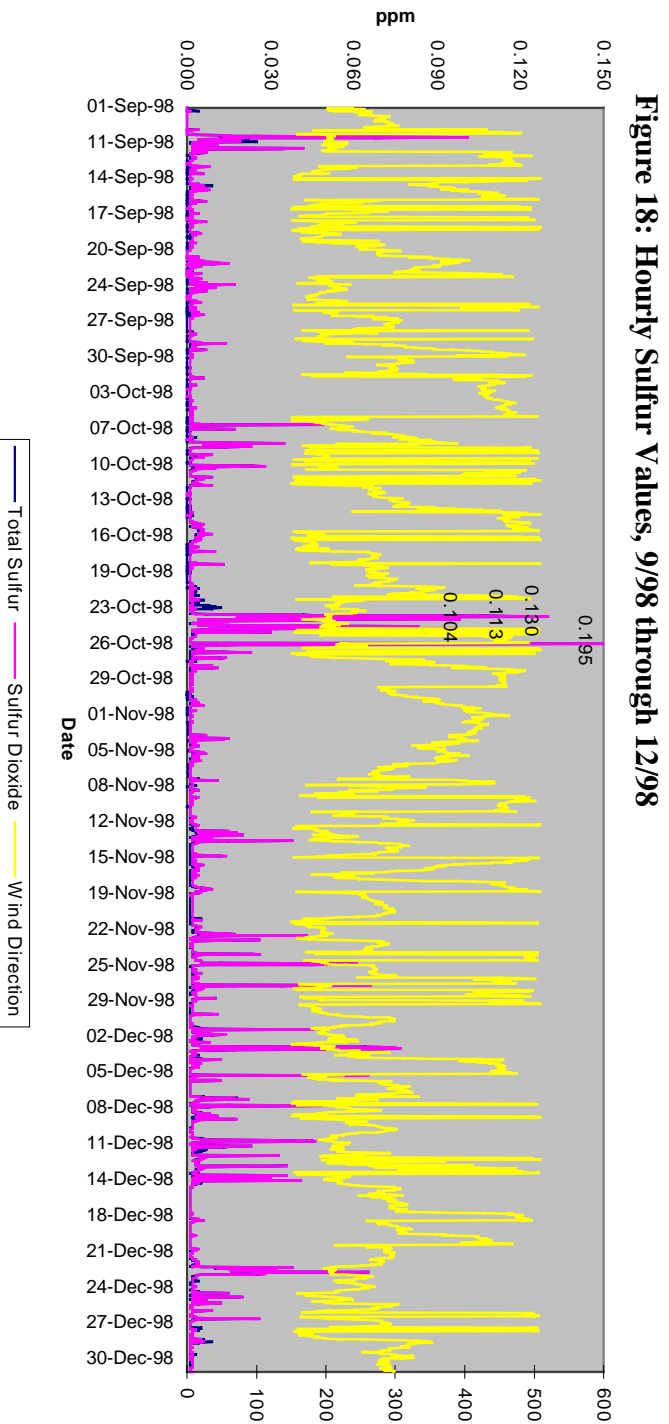
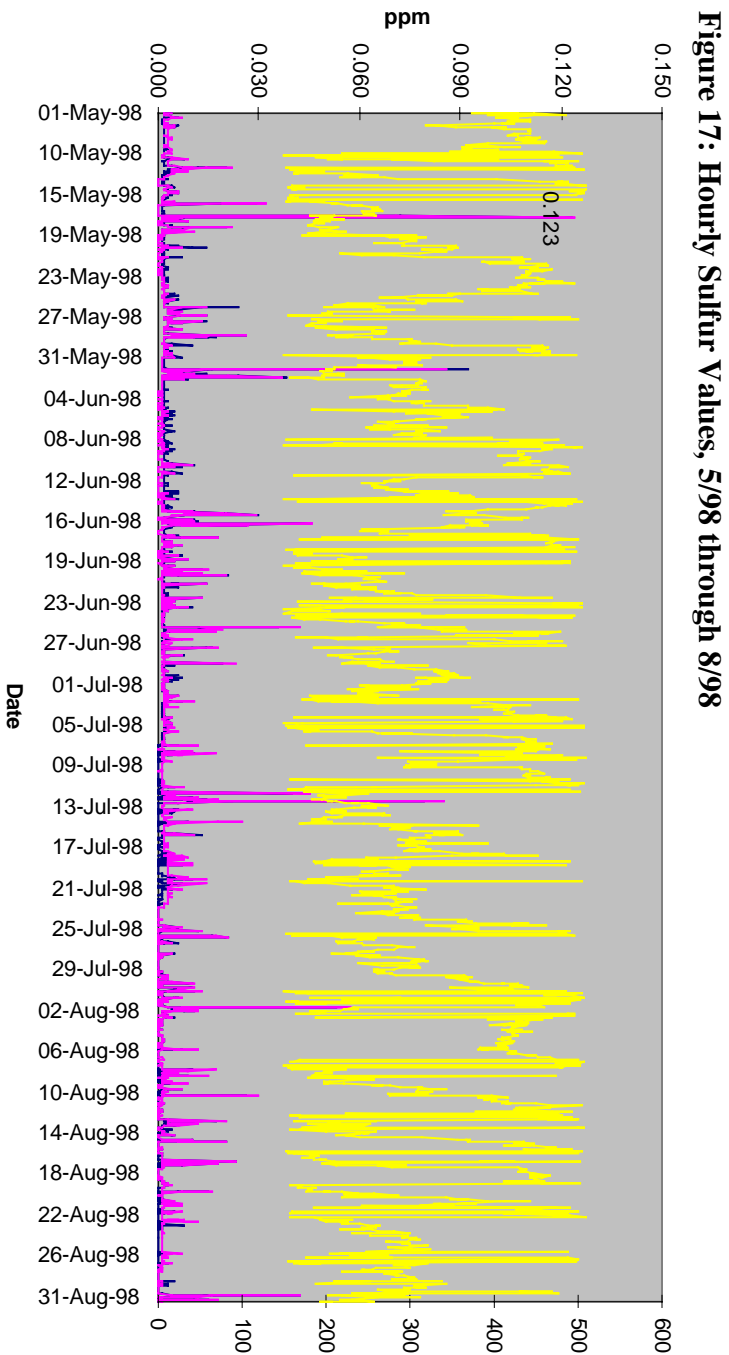


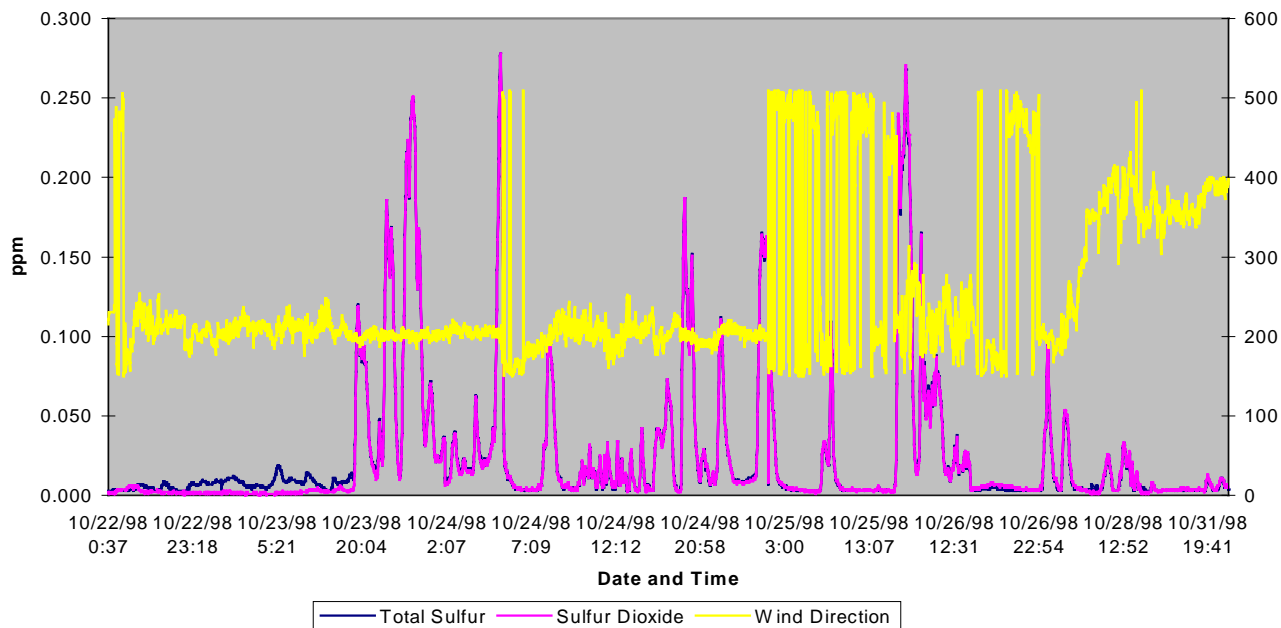
Figure 16: Hourly Sulfur Values, 12/97 through 4/98





The following figure illustrates the pollution episode in late October, 1998. Plotted are all minute averages greater than 0.002 ppm. This graph shows both a period of reduced sulfur gases (during 10/22 and the early part of 10/23), and a typical pattern for high value hours.

Figure 19: Significant Sulfur Event 10/22 – 11/1/98, Minute Average Values



Sulfur Gas Conclusions

Analysis of the total sulfur and SO₂ results yields the following pertinent points of interest:

1. The sulfur gases observed in Wisconsin Rapids are primarily SO₂.
2. No exceedences of the national 24-hour standard of 0.140 ppm have been recorded.
3. Occasional periods of discernible reduced sulfur compounds have been observed.
4. The odor of reduced sulfur compounds can be noticed below instrumental detection limits.

Recommendations

At the time of publication (June 1999), the WUATM site in Wisconsin Rapids has been operating for nearly 2 years. Another year of monitoring is recommended for this location. Three years of monitoring at the statewide metals sites will be complete at the end of June 1999. Numerous changes are recommended to both the parameter list and the statewide metals sites.

Semi-Volatile Organic Compounds

These compounds will continue to be monitored with the full site in Wisconsin Rapids and in Green Bay. However, our results show that most of the chlorinated pesticides on our parameter list are below method detection limits. As such, it is recommended that these compounds be dropped from regular monitoring and replaced with current use pesticides detectable with a Nitrogen Phosphorus detector.

The specific changes include dropping DDE, Dieldrin, cis- and trans- Chlordane, cis- and trans- Nonachlor, Heptachlor Epoxide and Lindane. These parameters will be replaced with Cyanazine, Simazine, Alachlor and Metolachlor. Atrazine will continue to be monitored. All pesticide parameters will be determined only between April and September. Total PCBs as Arochlor will continue to be determined as previously.

The possibility exists for further monitoring around the Fox River valley, in conjunction with the remediation efforts currently underway. Although significant increases in air-borne PCB are not anticipated as a part of this work, a monitoring presence can help insure that this is indeed the case.

Statewide Metals

The results of the statewide metals monitoring network to date have shown very few detects for Selenium and Vanadium. Since these are relatively minor toxic metals, it is recommended that these parameters be dropped from the list, and replaced with Nickel and Manganese. The choice of these two compounds is driven by several factors, including their significantly greater level of reported industrial emissions. Other factors brought to bear are the relative toxicity of Nickel and the potential of increased ambient Manganese if MMT (methylcyclopentadienyl manganese tricarbonyl) comes into common use as a fuel additive.

Three years of monitoring at the current sites provides sufficient data to determine current levels of these parameters. Based on our results, the Superior site appears to be consistently low. It is recommended that this site be discontinued.

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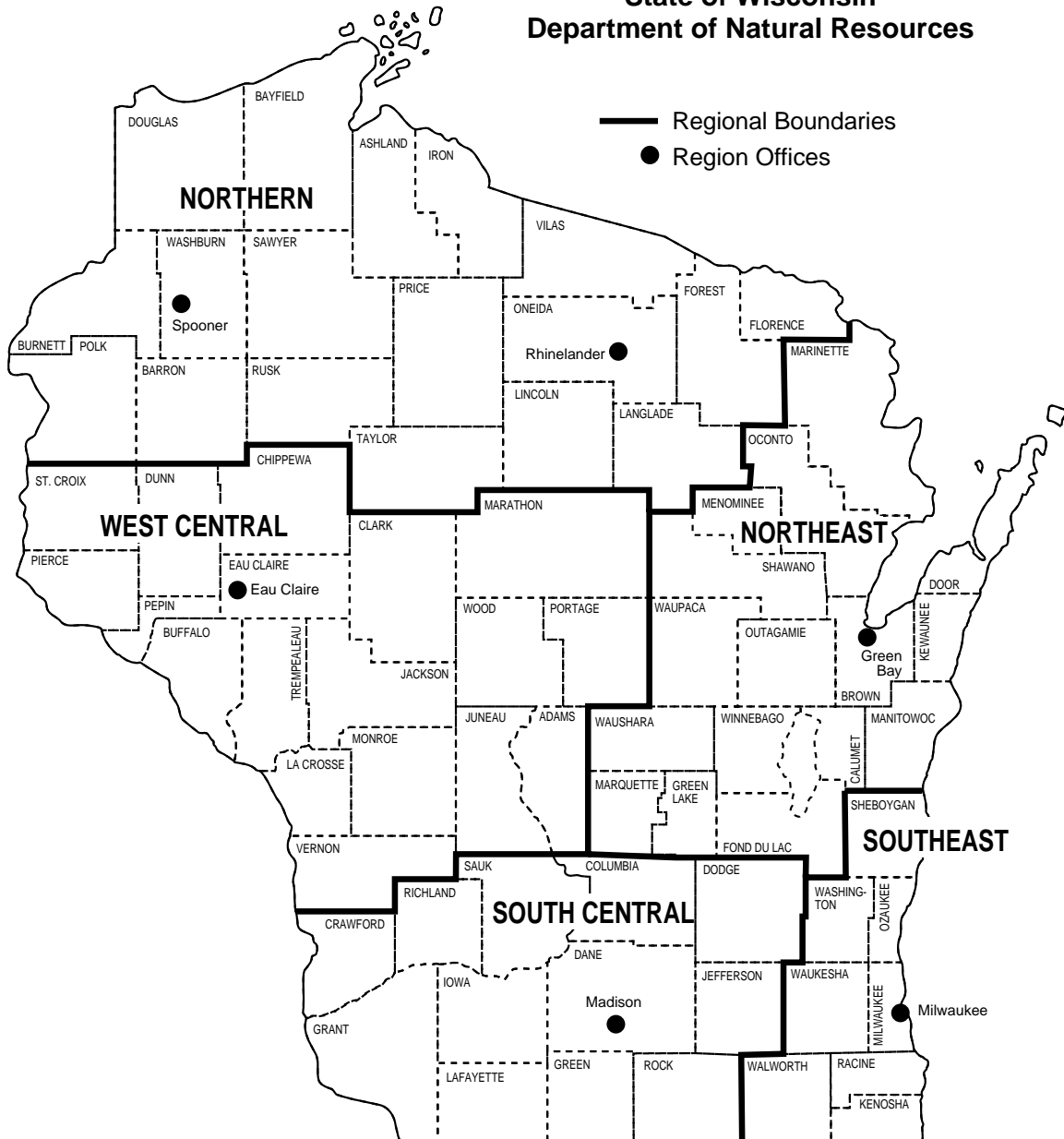
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**State of Wisconsin
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